PB84-104702

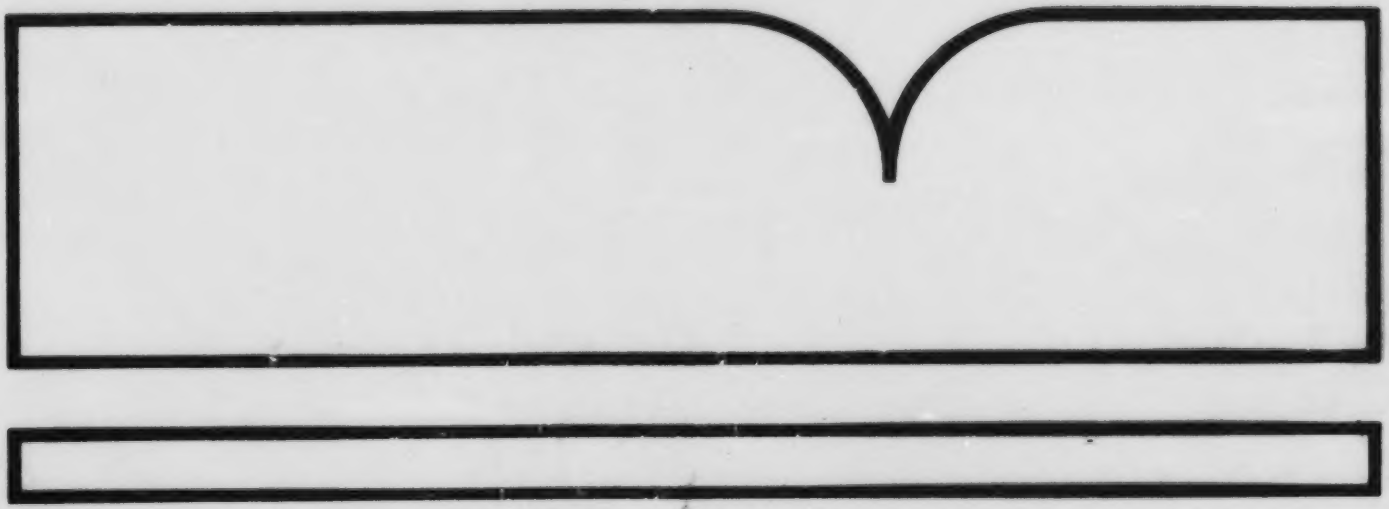
Calculation of Emissions and Fuel Economy when Using Alternate Fuels

Southwest Research Inst., San Antonio, TX

Prepared for

Environmental Protection Agency, Ann Arbor, MI

Mar 83



U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA 460/3-83-009		PB84 104702

4. TITLE AND SUBTITLE	5. REPORT DATE
CALCULATION OF EMISSIONS AND FUEL ECONOMY WHEN USING ALTERNATE FUELS	March 1983
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Charles M. Urban	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Southwest Research Institute 6220 Culebra Road San Antonio, Texas 78284	11. CONTRACT/GRANT NO. 68-03-3073
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Environmental Protection Agency Emission Control Technology Division 2565 Plymouth Road Ann Arbor, Michigan 48105	Final Report (5-82/9-82) 14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

16. ABSTRACT

This report provides methods for the calculation of vehicle emissions and fuel consumption when nonstandard fuels are used. Methods of analyses, required for evaluation of alternate fuels, are includes by reference or as Appendices to this report.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution Exhaust Emissions Chemical Analysis Motor Vehicle	Emissions Test Procedures	

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release Unlimited	Unclassified	98
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

United States
Environmental Protection
Agency

Office of Mobile Source Air Pollution Control
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, Michigan 48105

EPA 460/3-83-009
March 1983

Air

PB84-104702

EPA

Calculation of Emissions and Fuel Economy When Using Alternate Fuels

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

EPA 460/3-83-009

Calculation of Emissions and Fuel Economy When Using Alternate Fuels

by

Charles M. Urban

Southwest Research Institute
6220 Culebra Road
San Antonio, Texas 78284

Contract No. 68-03-3073
Work Assignment 8

EPA Project Officer: Robert J. Garbe

Prepared for

ENVIRONMENTAL PROTECTION AGENCY
Office of Mobile Source Air Pollution Control
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, Michigan 48105

March 1983

This report is issued by the Environmental Protection Agency to report technical data of interest to a limited number of readers. Copies are available free of charge to Federal employees, current contractors and grantees, and nonprofit organizations - in limited quantities - from the Library Services Offices, Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan, 48105.

This report was furnished to the Environmental Protection Agency by Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas, in fullfillment of Work Assignment 8 of Contract No. 68-03-3073. The contents of this report are reproduced herein as received from Southwest Research Institute. The opinions, findings, and conclusions expressed are those of the author and not necessarily those of the Environmental Protection Agency. Mention of company or product names is not to be considered as an endorsement by the Environmental Ptotection Agency.

Publication No. 460/3-83-009

FOREWORD

This Work Assignment was initiated by the Control Technology Assessment and Characterization Branch, Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan 48105. The effort on which this report is based was accomplished by the Department of Emissions Research of Southwest Research Institute, 6220 Culebra Road, San Antonio, Texas 78284. This program, authorized by Work Assignment 8 under Contract 68-03-3073, was initiated May 26, 1982 and was completed September 28, 1982. The program was identified within Southwest Research Institute as Project 05-6619-008.

This Work Assignment was conducted by Mr. Charles Urban, Project Leader. Mr. Charles Hare was Project Manager and was involved in the initial technical and fiscal negotiations and subsequent major program decisions. The EPA Project Officer was Mr. Robert J. Garbe of the Technical Support Staff, Environmental Protection Agency.

ABSTRACT

This report provides methods for the calculation of vehicle emissions and fuel consumption when nonstandard fuels are used. Methods of analysis, required for evaluation of alternate fuels, are included by reference or as Appendices to this report.

TABLE OF CONTENTS

	Page
FOREWORD	iii
ABSTRACT	iv
LIST OF ANALYTICAL METHODS AND CALCULATIONS	vi
I. INTRODUCTION	1
II. EQUIPMENT, INSTRUMENTATION AND ANALYTICAL METHODS	3
A. CVS Dilution Requirements	3
B. Emissions Instrumentation	4
C. Analytical Methods	4
III. FUEL COMPOSITION	7
A. Blends of Known Composition	7
B. Fuels of Unknown Composition	7
IV. EXHAUST EMISSIONS	11
A. Exhaust Organic Matter Composition	11
B. Calculation of Gaseous Exhaust Emissions	12
C. Calculation of Particulate Exhaust Emissions	20
D. Non-Methane Hydrocarbons	20
E. Unregulated Exhaust Emissions	20
V. FUEL ECONOMY	21
A. Calculation of Fuel Economy	21
B. Fuel Economy Related Considerations	23
VI. EVAPORATIVE EMISSIONS	25
A. Evaporative HC Composition for Hydrocarbon Fuels	25
B. Evaporative Organic Matter Composition for Other Fuels	26
C. Calculation of Evaporative Emissions	26
REFERENCES	27
SELECTED BIBLIOGRAPHY	28
APPENDICES	

LIST OF ANALYTICAL METHODS AND CALCULATIONS

	Page
CVS Dilution Requirements	3
CO_2 Emissions Concentrations	4
List of Analytical Methods	5
Component Fractions in Fuel Blends	8
Allowable Accuracies for Fuel Elemental Analysis	9
Calculation of Gaseous Exhaust Emissions	12
Example Emission Calculation for Methanol Fuel	18
Calculation of Particulate Exhaust Emissions	20
List of Possible Unregulated Emissions	20
Calculation of Fuel Economy	21
Example Fuel Economy Calculation for Methanol Fuel	23
Calculation of Energy Based Fuel Consumption	23
Calculation of Evaporative Emissions	26

I. INTRODUCTION

The objective of this Work Assignment was to compile and document procedures to follow when calculating and reporting exhaust or evaporative emissions data and carbon balance fuel economy data from vehicles operating on hydrogen and carbon containing fuels other than commercial gasoline and Diesel fuel.

This report describes calculational procedures for use in light-duty applications when using alternate fuels. In addition to the calculational changes that are required to the light-duty certification procedure, some equipment and instrumentation changes may also be required. Discussion of these equipment and instrumentation requirements is also included in this report.

The composition of the evaporative and the exhaust organic matter with alternate fuels generally differs from the composition of the hydrocarbons used to establish the HC emissions standard. The relationship between the organic matter value for an alternate fuel and the HC emissions value for a standard gasoline or diesel fuel have not been established. Therefore, no procedure is included for the calculation of a single composite value for organic matter when alternate fuels are used.

The format used for mathematical equations in this report is in accordance with that used in the Code of Federal Regulation.[1]* Computations are to be performed in accordance with the IBM hierarchy of operations.

Although specific application to the heavy-duty transient procedure is not included, the procedures given are generally applicable. The methods given can be fairly readily adapted for use with the heavy-duty transient procedure.

*Numbers in parentheses designate references at the end of this report.

II. EQUIPMENT, INSTRUMENTATION AND ANALYTICAL METHODS

Fuels having higher hydrogen-to-carbon ratios produce more water and less CO_2 for equal energy output. Therefore, a higher than normal CVS dilution flow rate could be required to keep water condensation from occurring. A higher CVS flow rate (CO_2 emissions would also be directly affected by lower CO_2 production) could result in emissions concentrations that are lower than the prescribed accuracies of the normally used emissions instruments. Therefore, the CVS flow rate and the exhaust emissions instrumentation are essential considerations when alternate fuels are to be evaluated.

A. CVS Dilution Requirements

The CVS flow capacity of 300 to 350 scfm that is designated in the light-duty certification procedure as being adequate, is based on currently formulated gasoline and Diesel fuels.(1) Fuels containing a higher hydrogen-to-carbon ratio produce more water and can require a higher CVS dilution flow rate to keep condensation of water from occurring in the sample bags. Since the currently specified CVS flow rate generally prevents water condensation from occurring, when using gasoline or Diesel fuel, the CVS flow rate for an alternate fuel that is sufficient for most light-duty vehicles can be estimated as follows:

- $ACVSFR = (AFFH/ALHV) \times 5 \times 10^7$

  Where:
  - ACVSFR = CVS flow rate for alternate fuel that is sufficient for most vehicles, cfm
  - AFFH = Fuel fraction hydrogen of the alternate fuel
  - ALHV = Lower heating value of the alternate fuel, Btu/lg

The resulting flow rate (ACVSFR), however, is often much higher than is actually required, especially for smaller, fuel efficient vehicles. Therefore, the determination of the actual required CVS flow rate is given as follows:

- $RCVSFR = 16.6 \times AMPH \times FDEN \times FFH / (MPG \times (SSH - TSH))$

  Where:
  - RCVSFR = Required CVS flow rate, scfm
  - AMPH = Average speed, mph (16 minimum for the cycles of the FTP)
  - FDEN = Density of the fuel, g/mℓ
  - FFH = Fuel fraction hydrogen, mass/mass
  - MPG = Fuel economy, mpg
  - SSH = Specific humidity of saturated air at minimum sample bag temperature, lb/lb
  - TSH = Actual specific humidity of the dilution air at test conditions, lb/lb

  Note: Derivation of RCVSRF is given in Appendix A-1.

Combining the provisions in the ACVSFR and the RCVSFR equations, and making several assumptions to enable simplification, results in the following equation for estimation of the required CVS flow rate for the FTP:

$$ECVSFR = 45{,}000 \times FDEN \times FFH / MPG$$

When the fuel economy for the vehicle is not known, it can be estimated using the fuel economy for a similar vehicle operating on certification fuel multiplied by the ratio of the lower heating values per unit volume:

$$AMPG \simeq CMPG \times CLHV / ALHV$$

Where:

AMPG = Fuel economy with the alternate fuel, mpg
CMPG = Fuel economy with certification fuel, mpg
CLHV = Lower heating value of certification fuel (18,300 Btu/lb)[2]
ALHV = Lower heating value of the alternate fuel

B. Emissions Instrumentation

When fuels with high hydrogen-to-carbon ratios are used, emissions instrumentation having lower ranges may be required. Unless the emission rates are known, however, the necessary instrument ranges can not be predetermined. Therefore, the recommendation is that applicability of ranges be determined from actual measuremnt of emissions at the onset of testing.

CO_2 emission concentrations, however, can be estimated using the CVS flowrate, the carbon fraction of the fuel, and the fuel consumption on a weight basis. The equation, derived in Appendix A-2, is as follows:

$$CO_2\% = (451 \times AMPH \times FDEN) / (FE \times CVSFR)$$

Where:

$CO_2\%$ = CO_2 concentration in the Dilute Exhaust Sample, Percent
AMPH = Average Speed of the Cycle, mph
FDEN = Fuel Density, g/mℓ
FE = Cycle Fuel Economy, mpg
CVSFR = Flowrate of the CVS, scfm

C. Analytical Methods

In several of the calculations required for alternate fuels, additional analyses of the fuel or the emissions are specified or recommended. Some analytical methods are listed on the following page.

Method	Source
Determination of FID Response Factor	Appendix A-3
Measurement of Aldehydes and Ketones	Appendix A-4[3]
Measurement of Individual Hydrocarbons	Reference 3
Methane Measurement Using Gas Chromatograph	SAE J1151a[4]

Additional methods for special applications are listed as follows:

Method	Source
Measurement of Methanol	Appendix A-5[5]
Measurement of Ethanol	Appendix A-6[6]
Measurement of Tertiary Butyl Alcohol	Reference 6

III. FUEL COMPOSITION

In the procedure for certification of light-duty vehicles, a specified hydrogen-to-carbon ratio and density are assumed to be applicable for all petroleum based fuels meeting the prescribed specifications. When using alternate fuels, however, the differences in fuel composition and density are sufficiently large to make it essential that the actual values be determined and used.

The calculations of emissions and fuel economy, for alternate fuels, require the use of the weight ratios of carbon, hydrogen, oxygen, and the sum of the other elements in the fuel. For the calculation of fuel economy, the density of the fuel is also required.

For blends of known composition, the weight ratios of the constituents can either be measured or calculated. For fuels of unknown composition, however, determination of the elemental composition is essential. Due to the uncertainties involved when various liquids are blended together, it is recommended that fuel density always be determined by actual measurement (unless the effects of blending on density are specifically known for the specific blended fuel).

For gaseous fuels, such as propane, a significant quantity of impurities (e.g., CO_2) may be present in the fuel which would have an impact on the emissions and fuel economy calculations. Therefore, it is also important to determine the weight ratios of carbon, hydrogen, oxygen, and the sum of the other elements when gaseous fuels are used.

A. Blends of Known Composition

When blending a fuel of known composition, the elemental weight ratios can be determined by calculation. The method will be demonstrated using a blend of a gasoline, meeting the certification fuel specifications, and methanol (assuming such a blend is achieved).

For gasoline, a hydrogen-to-carbon ratio (HCR) of 1.85 to 1 can be assumed. This results in fuel carbon and hydrogen fractions of weight (GFC and GFH) of 0.866 and 0.134, respectively. Methanol has an MFC and MFH of 0.375 and 0.126, respectively. The remaining component in methanol is oxygen, with an MFO of 0.499. The resulting carbon, hydrogen, and oxygen fractions in a blend of gasoline and methanol are on the following page.

$$BFX = ((Wt\%\ Gas) \times GFX + (Wt\%\ Meth) \times MFX)/100\%$$

$$\text{Where: } Wt\%\ Gas = \frac{(Vol.\%\ Gas) \times GDEN \times 100}{(Vol.\%\ Gas) \times GDEN + (Vol.\%\ Meth) \times MDEN}$$

B, G, & M = Blend, Gasoline and Methanol
X = Carbon, hydrogen or oxygen
DEN = Density, g/mℓ

Assume 90% Gasoline and 10% Methanol by Weight:

$BFC = (90 \times 0.866 + 10 \times 0.375)/100 = 0.817$
$BFH = (90 \times 0.134 + 10 \times 0.126)/100 = 0.133$
$BFO = (90 \times 0.000 + 10 \times 0.499)/100 = 0.050$

The elemental fractions in a blended fuel can also be determined by elemental analyses of the fuel blend. Methods for such analyses are discussed in the following Section III.B. Due to the uncertainties involved in blending fuels, it is recommended that generally the density of the resultant fuel blend be determined by actual measurement.

B. Fuels of Unknown Composition

For fuels of unknown composition, the elemental fractions can be determined only by actual analysis. The carbon, hydrogen and oxygen values, and occasionally the nitrogen value, are required. Analysis of liquid fuels for these elements is extremely difficult, and standard ASTM methods are not currently available. It is recommended that such analysis be conducted only by a laboratory known to have the necessary expertise.

There does not appear to be general agreement on the best methods of analysis for these elements. The commerically available C, H, N, O and S analyzers were not specifically designed for, and do not generally appear to provide, satisfactory analysis of liquid fuels. Therefore, such analyzers are not a simple solution to the measurement problem and their use should be approached with caution.

Some example methods of elemental analysis for liquid fuels are as follows: Carbon and hydrogen have been satisfactorily measured using an elemental analyzer, or gravimetrically using a modified ASTM D-3178 method. Nitrogen has been satisfactorily measured using pyrochemiluminescence. Oxygen has been satifactorily measured using neutron activation analysis. In all cases, it appears that a very high level of expertise is essential to obtaining satisfactory analysis of these elements in liquid fuels.

For general quidance purposes, the accuracies of the analyses should be within the following limits:

Element	Analysis Accuracy as: % of Value[a]	% of Fuel[a]
Carbon	±0.5	±0.3
Hydrogen	±0.5	±0.3
Oxygen	±(0.2/Value[b] + 0.3)	±(0.2 + 0.3×Value[b])
Nitrogen	±(0.2/Value[b] + 0.3)	±(0.2 + 0.3×Value[b])
Total of All	--	1.0

[a] Use the analysis accuracy having the lowest absolute number

[b] Value as a weight fraction of total fuel

The limits given represent the extremes; an effort should be made to obtain better analysis accuracies than these extreme limits given.

The total of the weight fractions of the C, H, O and N in the fuel may not add up to a total of 1.000. Computer inputs include the fuel fraction of C, H, O and other elements. If the total for C, H, O and N is less than 1.000, add the difference to the value for other elements. If the total for C, H, O and N is greater than 1.000, subtract the difference from the value for oxygen (O) or the value for other elements, as appropriate.

The acceptable level of sulfur is generally sufficiently low so that the amount of sulfur present does not significantly affect the standard emissions and fuel consumption calculations. Amount of sulfur in the fuel, however, is generally considered to be of sufficient importance to justify determination of sulfur. Depending on the type of fuel involved and its source, it may also be worthwhile to include additional analyses, such as ash content, gum, and some additional specific elements. Standard ASTM methods are available for sulfur, ash, gum, and several specific elements.

IV. EXHAUST EMISSIONS

The basic calculations used in the certification of light-duty vehicles are applicable for use with alternate fuels. A number of the parameters utilized, however, must be changed to account for the potentially large differences in fuel and exhaust organic matter composition. In addition, no generally acceptable method is currently available for determination of a meaningful composite value for the organic matter when using alternate fuels. This section describes the determination of the required parameters and the calculational methods to enable incorporation of these parameters.

A. Exhaust Organic Matter Composition

The composition of the exhaust hydrocarbon emissions affects the response factor of the FID instrument and the density of the HC emissions. The current light-duty certification procedure assumes that the overall FID resposne factor for the hydrocarbons in the exhaust is essentially equal to the FID response factor for propane. For alternate fuels with significantly different composition such response factor assumption is inappropriate.

The only method determined to be generally acceptable for alternate fuels is to measure the individual components of the organic matter in the exhaust, and then to calculate and report all of the major constituents. Unfortunately, this method is impractical in many situations. Therefore, it is recommended that measurement, calculation, and reporting of the individual components of the exhaust organic matter be done to the extent practical. Generally, the summation of the individual components is inappropriate, and should not be done, when alternate fuels are used.

In cases where an exact determination is not essential, a simpler determination can be made by assuming the composition of the organic matter in the exhaust is equal to that in the fuel. Determine the FID response factor for the fuel using the method given in Appendix A-3, and apply this factor to the FID measured value of the exhaust. The method used for determination of organic matter should always be identified for any such data reported.

B. Calculation of Gaseous Exhaust Emissions

The following calculations for exhaust emissions are recommended for use when non-standard carbon bearing fuels are utilized. These calculations are based on the calculations given in 40 CFR Part 86, Subpart B, §86.144-78, with latest revisions incorporated. The basic format used in §86.144 has been retained. Changes or additions to the calculational methods in §86.144-78 are identified by asterisk(*) and are derived in Appendix B-2.

*Analyses, in addition to those required in the certification procedure are as follows:

Composition of the Fuel

FFC = Fuel fraction carbon by weight
FFH = Fuel fraction hydrogen by weight
FFO = Fuel fraction oxygen by weight
FFX = Fuel fraction of other elements by weight

The following is based on §86.144-78 Calculations; exhaust emissions.

The final reported test results shall be computed by use of the following formula:

(a) For light-duty vehicles and light-duty trucks:

$$Y_{wm} = 0.43((Y_{ct} + Y_s)/(D_{ct} + D_s)) + 0.57((Y_{ht} + Y_s)/(D_h + D_s))$$

Where:

Y_{wm} = Weighted mass emissions of each pollutant, i.e.; HC, CO, NO_2, CO_2 in grams per vehicle mile.

Y_{ct} = Mass emissions as calculated from the "transient" phase of the cold start test, in grams per test phase.

Y_{ht} = Mass emissions as calculated from the "transient" phase of the hot start test, in grams per test phase.

Y_s = Mass emissions as calculated from the "stabilized" phase of the cold start test, in grams per test phase.

D_{ct} = The measured driving distance from the "transient" phase of the cold start test, in miles.

D_{ht} = The measured distance from the "transient" phase of the hot start test, in miles.

D_s = The measured driving distance from the "stabilized" phase of the cold start test, in miles.

(b) The mass of each pollutant for each phase of both the cold start test and the hot start test is determined from the following:

(1) Organic matter mass (to be calculated individually for each major component of organic matter in the exhaust).

$$OM_{mass} = V_{mix} \times Density_{OM} \times (OM_{conc}/1{,}000{,}000)$$

(2) Oxides of nitrogen mass:

$$NO_{xmass} = V_{mix} \times Density_{NOx} \times K_H \times (NO_{xconc}/1{,}000{,}000)$$

(3) Carbon monoxide mass:

$$CO_{mass} = V_{mix} \times Density_{CO} \times (CO_{conc}/1{,}000{,}000)$$

(4) Carbon dioxide mass:

$$CO_{mass} = V_{mix} \times Density_{CO2} \times (CO_{2conc}/100)$$

(c) Meaning of symbols:

(1) OM_{mass} = Organic matter emissions, in grams per test phase.

$Density_{OM}$ = 14.135/EFC g/ft^3(0.4493/EFC kg/m^3)

Based on: Density of hydrocarbons is 16.33 g/ft^3(0.5768 kg/m^3), assuming an average carbon-to-hydrogen ratio of 1:1.85, at 68°F(20°C) and 760 mm Hg (101.3 kPa) pressure.

Where:

*EFC = Fraction carbon in exhaust organic matter.

*OM_{conc} = Organic matter concentration of the dilute exhaust sample corrected for background in ppm carbon equivalent.

Where:

$OM_{conc} = OM_c - OM_d(1-1/DF)$

Where:

OM_c = Organic matter concentration of the dilute exhaust sample or, for Diesel, average organic matter concentration of dilute exhaust sample as calculated from the integrated OM traces, in ppm carbon equivalent.

OM_d = Organic matter concentration of the dilution air as measured, in ppm carbon equivalent.*

(2) NO_{xmass} = Oxides of nitrogen emissions, in grams per test phase.

$Density_{NO2}$ = Density of oxides of nitrogen is 54.16 g/ft^3(1.913 kg/m^3) assuming they are in the form of nitrogen dioxide, at 68°F(20°C) and 760 mm Hg (101.3 kPa) pressure.

NO_{xconc} = Oxides of nitrogen concentration of the dilute exhaust sample corrected for background, in ppm.

$$NO_{xconc} = NO_{xc} - NO_{xd}(1 - 1/DF)$$

Where:
NO_x = Oxides of nitrogen concentration of the dilute exhaust sample as measured, in ppm.

NO_{xd} = Oxides of nitrogen concentration of the dilution air as measured, in ppm.

(3) CO_{mass} = Carbon monoxide emissions, in grams per test phase.

$Density_{CO}$ = Density of carbon monoxide is 32.97 g/ft^3(1.164 kg/m^3), at 68°F(20°C) and 760 mm Hg (101.3 kPa) pressure.

CO_{conc} = Carbon monoxide concentration of the dilute exhaust sample corrected for background, water vapor, and CO_2 extraction, in ppm.

$$CO_{conc} = CO_c - CO_d(1 - 1/DF)$$

Where:
CO_c = Carbon monoxide concentration of the dilute exhaust sample volume corrected for water vapor and carbon dioxide extraction, in ppm.

$$*CO_c = (1 - (0.01 + 0.005 \times HCR)\ CO_{2c} - 0.000323R)CO_{cm}*$$

Where:
CO_{cm} = Carbon monoxide concentration of the dilute exhaust sample as measured, in ppm.

CO_{2c} = Carbon dioxide concentration of the dilute exhaust sample, in percent.

R = Relative humidity of the dilution air, in percent (see §86.142(n)).

*HCR = Hydrogen-to-carbon ratio of the fuel
= (FFH/1.008)/(FFC/12.011)*

CO_d = Carbon monoxide concentration of the dilution air corrected for water vapor extraction, in ppm.

$$CO_d = (1 - 0.000323R)CO_{dm}$$

Where:
CO_{dm} = Carbon monoxide concentration of the dilution air sample as measured, in ppm.

Note: If a CO instrument which meets the criteria specified in §86.111 is used and the conditioning column has been deleted, CO_{cm} can be substituted directly for CO_c and CO_{dm} can be substituted directly for CO_d.

(4) CO_{2mass} = Carbon dioxide emissions, in grams per test phase.

$Density_{CO_2}$ = Density of carbon dioxide is 51.81 g/ft^3 (1.830 kg/m^3), at 68°F(20°C) and 760 mm Hg(101.3 kPa)

CO_{2conc} = Carbon dioxide concentration of the dilute exhaust sample corrected for background, in percent.

$$CO_{2conc} = CO_{2c} - CO_{2d}\ (1 - 1/DF)$$

Where:

CO_{2d} = Carbon dioxide concentration of the dilution air as measured, in percent

(5) $$*DF = SPCO_2/[CO_{2c} + (\Sigma OM_c + CO_c)10^{-4}]*$$

Where:

$*SPCO_2$ = Stoichiometric percent of CO_2 in undiluted exhaust
$= (FFC/(FFC + 5.958\ FFH + 12.011 \times FFX/MWX + 0.3278 \times SAFR)) \times 100*$

$*\Sigma OM_c$ = Summation of the individual components of the organic matter in ppm carbon equivalent. (A value for organic matter as measured by FID can generally be used for ΣOM_c when OM_c by FID divided by $(CO_{2c} + CO_c)$ is less than 0.02).

FFX and MWX are the fuel fraction and the molecular weight, respectively, of any unknown compound in the fuel. If FFX is less than 0.03 and MWX can not readily be determined, assume MWX = 28.162.

Where:

$*SAFR$ = Stoichiometric air to fuel ratio
$= 11.514 \times FFC + 34.298 \times FFH - 4.322 \times FFO*$

K_H = Humidity correction factor.

$K_H = 1/[1 - 0.0047(H - 75)]$
for SI units $= 1/[1 - 0.0329(H - 10.71)]$

Where:

H = Absolute humidity in grains (grams) of water per pound (kilogram) of dry air.

$H = [(43.478)R_c \times R_d]/[P_B - (P_d \times P_c/100)]$
for SI units, $H = [(6.211)R_c \times R_d]/P_B - (P_d \times R_d/100)]$

R_a = Relative humidity of the ambient air, in percent.

P_d = Saturated vapor pressure, in mm Hg (kPa) at the ambient dry bulb temperature.

P_B = Barometric pressure, in mm Hg (kPa).

V_{mix} = Total dilute exhaust volume in cubic feet per test phase corrected to standard conditions of 528°F (293°K) and 760 mm Hg (101.3 kPa).

For PDP - CVS, V_{mix} is:

$$V_{min} = V_o \times \frac{N(P_B - P_4)\ 528\ R}{(760\ mm\ Hg)\ (T_p)}$$

for SI units,

$$V_{mix} = V_o \times \frac{N(P_B - P_4)(293.15\ K)}{(101.325\ kPa)(T_D)}$$

Where:

V_o = Volume of gas pumped by the positive displacement pump, in cubic feet (m^3) per revolution. This volume is dependent on the pressure differential across the positive displacement pump.

N = Number of revolutions of the positive displacement pump during the test phase while samples are being collected.

P_B = Barometric pressure, in mm Hg (kPa).

P_d = Pressure depression below atmospheric measured at the inlet to the positive displacement pump, in mm Hg (kPa) (during an Idle mode).

T_P = Average temperature of dilute exhaust entering positive displacement pump during test, R(K).

(d) Example calculation of mass values of exhaust emissions using positive displacement pump and Indolene fuel of $CH_{1.85}$. For Indolene Fuel, the exhaust organic matter are hydrocarbons).

(1) For the "transient" phase of the cold start test assume the following:
V_o = 0.29344 ft^3/revolution; N = 10,485; R = 48.0 percent;
R_a = 48.2 percent; P_B - 762 mm Hg; P_d = 22.225 mm Hg; P_4 = 70 mm Hg;
T_P = 570 R; HC_c = 105.8 ppm, carbon equivalent; NO_{xc} = 11.2 ppm;
CO_{cm} = 306.6 ppm; CL_c = 1.43 percent; HC_d = 12.1 ppm; NO_{xd} = 0.8 ppm;
CO_{dm} = 15.3 ppm.

CO_{2d} = 0.032 percent; D_{ct} = 3.598 miles;

*FFC = 0.8656; FFH = 0.1344;
FFO = 0; FFX = 0; FID Response Factor = 1.0.*

Then:
V_{mix} = (0.29344)×(10.485)×(762 - 70)×
(528)/(760)(570) = 2595.0 ft^3 per test phase.

H = (43.478) (48.2) (22.225)/[782 - (22.225×48.2/100))]
= 62 grains of water per pound of dry air.

K_H = 1/[1 - 0.0047(62 - 75)] = 0.9424

HCR = (0.1344/1.008)/(0.8656/12.011) = 1.85

*CO_c = (1 - (0.01 + 0.005×1.85)1.43 - 0.000323×48)306.6 = 293.4 ppm

CO_d = (1 - 0.000323×48)15.3 = 15.1 ppm

SAFR = 11.514×0.8656 + 34.298×0.1344 = 14.576

$SPCO_2$ = (0.8656/(0.8656 + 5.958×0.1344 + 0.3278×14.576))×100 = 13.4

DF = 13.4[1.43 + (105.8/1.0 + 293.4)×10^{-4}] = 9.116

HC_{cc} = 105.8 - 12.1(1 - 1/9.116) + 95.03 ppm.

HC_{conc} = HC_{cc}/1.0 = 95.03 ppm

Density HC = 14.135/0.8656 = 16.33 g/ft^3

HC_{mass} = (2595)(16.33)(95.03/1,000,000) = 4.027 grams per test phase

NO_{xconc} = 11.2 - 0.8(1 - 1/9.116) = 10.49 ppm

NO_{xmass} = (2595)(54.16)(10.49/1,000,000)(0.9424) = 1.389 gram per test phase.

CO_{conc} = 293.4 - 15.1(1 - 1/9.116) = 280.0 ppm

CO_{mass} = (2595)(32.97)(280/1,000,000) = 23.96 grams per test phase

CO_{2conc} = 1.43 - 0.032(1 - 1/9.116) = 1.402%

CO_{2mass} = (2595.0)(51.85)(1.402/100) = 1886 grams per test phase.

(2) For the stabilized portion of the cold start test assume that similar calculations resulted in the following:

HC_{mass} = 0.62 grams per test phase

NO_{xmass} = 1.27 grams per test phase

CO_{mass} = 5.98 grams per test phase

CO_{2mass} = 2346 grams per test phase

D_s = 3.902 miles

(3) For the "transient" portion of the hot start test assume that similar calculations resulted in the following:

HC_{mass} = 0.51 grams per test phase

NO_{xmass} = 1.38 grams per test phase

CO_{mass} = 5.01 grams per test phase

CO_{2mass} = 1758 grams per test phase

D_{ht} = 3.598 miles

(4) Weighted mass emission results:

HC_{wm} = 0.43[(4.027 + 0.52)/(3.598 + 3.902)] + 0.57[(0.51 + 0.62)/(3.598 + 3.902)] = 0.352 grams per vehicle mile.

NO_{xwm} = 0.43[(1.389 + 1.27)/(3.598 + 3.092)] + 0.57[1.38 + 1.27)/(3/598 + 3.902)] = 0.354 grams per vehicle mile.

CO_{wm} = 0.43[(23.96 + 5.98)/(3.598 + 3.902)] + 0.57[5.01 + 5.98)/(3.598 + 3.902)] = 2.55 grams per vehicle mile.

CO_{2wm} = 0.32[(1886 + 2346)/(3.598 + 3.902)] + 0.57 [(1758 + 2346)/(3.598 + 3.902)] = 555 grams per vehicle mile

*(e) Example calculation of mass values of exhaust emissions when using methanol fuel (CH_4O). All inputs except for fuel composition and exhaust organic matter are assumed to be the same as in previous example (d).

(1) Fuel composition is as follows:

FFC = 0.375; FFH = 0.126; FFO = 0.499;

Then:

V_{mix} = 2595.0 ft^3

K_H = 0.9424

HCR = (0.126/1.008)/0.375/12.011) = 4.00

CO_c = (1 - (0.01 + 0.005×4.00)1.43 - 0.000323×48)306.6 = 288.7 ppm

CO_d = 15.1 ppm

$SAFR = 11.514 \times 0.375 + 34.298 \times 0.126 - 4.322 \times 0.499 = 6.48$

$SPCO_2 = (0.275/(0.375 + 5.958 \times 0.126 + 0.3278 \times 6.482)) \times 100 = 11.54$

$(OM_c \text{ by FID})/(CO_{2c} + CO_c) = 105.8/(1.43 \times 10^4 + 288.7) = 0.007 < 0.02.$

Therefore:

$DF = 11.54/[1.43 + (105.8 + 288.7) \times 10^{-4}] = 7.84$

$Density_{OM} = 14.135/0.375 = 37.69 \text{ g/ft}^3$

OM_{conc} = (Data are not available)

OM_{mass} = (can not be determined from available data)

(OM_{mass} by FID = (2595)(37.69)(105.8/1,000,000) = 10.35 grams per test phase).

$NO_{x_{conc}} = 11.2 - 0.8(1 - 1/7.84) = 10.50$ ppm

$NO_{x_{mass}} = (2595)(54.16)(10.51/1,000,000)(0.9424) = 1.391$ grams per test phase.

$CO_{conc} = 288.7 - 15.1(1 - 1/7.84) = 275.5$ ppm

$CO_{mass} = (2595)(32.97)(275.5/1,000,000) = 23.57$ grams per test phase.

$CO_{2_{conc}} = 1.43 - 0.032(1 - 1/7.84) = 1.402\%$

$CO_{2_{mass}} = (2595.0)(51.85)(1.402/100) = 1886$ grams per test phase.*

Assume 100.0 ppm of methanol was measured in the exhaust using the method given in Appendix A-5:

$Methanol_{mass} = (2595)(37.69)(100.0/1,000,000) = 9.781$ gram per test phase

Note: Other components of organic matter may also be present in the exhaust; these should be determined and reported to the extent practical.

C. Calculation of Particulate Exhaust Emissions

Use of an alternate fuel does not affect the procedure or the calculations for diesel particulate emissions. Therefore, the procedure and the calculations for diesel particulate given in 40 CFR, Part 86, Subpart B can be used, without modification.

D. Non-Methane Hydrocarbons

Consideration has been given by the EPA to basing the HC emissions standard on non-methane hydrocarbons. This, however, has not been done, but remains under consideration. Therefore, for the present, it is recommended that the composition of the exhaust HC be defined to the extent practical (e.g., with methanol fuel, measure exhaust for methanol, aldehydes, and methane). Such data could provide input for future decisions as more becomes known about individual hydrocarbon photochemical reactivity.

E. Unregulated Exhaust Emissions

It has been determined that some alternate fuels may be prone to produce higher levels of some currently unregulated emissions (e.g., alcohol fuels tend to produce higher levels of aldehydes). At the present time, the only specific recommendation is to include the analyses of aldehydes and the specific alcohol, when an alcohol fuel is used.

Other emissions to measure for, if any, should be based on the composition of the fuel and on whichever emission(s) is (are) considered to be of sufficient importance at the time. No specific recommendations can be provided, but some general guidance can be given. Under certain operating conditions the following relationships might occur:

Fuel Description	Other Exhaust Emissions to Consider	Source for Analytical Method
Methanol	aldehydes (primarily formaldehyde)	Appenidx A-4
	unburned methanol	Appendix A-5
Ethanol	aldehydes (primarily acetaldehyde)	Appendix A-4
	unburned ethanol	Appendix A-6
High sulfur	sulfate	Reference 3
	sulfur dioxide	Refreence 3
High aromatic (diesel)	phenols	Reference 7
	nitropyrenes	Reference 8
	Ames response	Reference 9
High Nitrogen (diesel)	nitropyrenes	Reference 8
	Ames Response	Reference 9

V. FUEL ECONOMY

The procedure for determination of fuel economy, given in the fuel Economy Regulations,[9] can be made applicable for use with alternate fuels by incorporating the actual carbon fraction and density of the fuel. For alternate fuels, however, the resulting expression of fuel economy, in terms of distance traveled per unit volume of fuel used, is not sufficient to enable making meaningful comparisons. Therefore, an additional method for expression of fuel economy (consumption) has been selected and its use is recommended.

A. Calculation of Fuel Economy

The following calculations for fuel economy are recommended for use when non-standard carbon containing fuels are utilized. These calculations are based on the method given in 40 CFR Part 600, Subpart B, §600.113-78 and Appendix II, with latest revisions incorporated. The basic format used in §600.113 has been retained. Changes or additions to the calculation method in §600-113-78 are identified by asterisk(*). A required analysis, in addition to those required in §600.113 or in the previous calculation procedure for exhaust emissions given in Section IV of this report, is the density of the fuel.

The following is based on §600-113-78 Fuel economy calculations.

The calculations of vehicle fuel economy values require the weighted grams/mile values for OM, CO, and CO_2. (OM = Organic matter).

(a) Calculate the weighted grams/mile values for the city fuel economy test for OM, CO, and CO_2 as specified in the modifications to §86.144 as given in Section IV.B. of this report.

(b)(1) Calculate the mass values for the highway fuel economy test for OM, CO, and CO_2 as specified in modifications to paragraph (b) of §86.144 as given in Section IV.B. of this report.

(2) Calculate the grams/mile values for the highway test for OM, CO, and CO_2 by dividing the mass values obtained in (b)(1) by the actual distance traveled, measured in miles, as specified in paragraph (h) of §86.135.

(c) Calculate the city fuel economy and highway fuel economy from grams/mile values for OM, CO, and CO_2. The OM values (obtained per paragraph (a) or (b) as applicable) used in each calculation in this section are rounded to the nearest 0.01 grams/mile. The CO values (obtained per paragraph (a) or (b) as applicable) used in each calculation in this section are rounded to the nearest 0.1 grams/mile. The CO_2 values (obtained per paragraph (a) or (b) of this section as applicable) used in each calculation in this section are rounded to the nearest gram/mile.

(d) and (e) Calculate the fuel economy in miles per gallon of gasoline by dividing the grams of carbon per gallon of fuel (GCPG) by the sum of three terms:

*Where: GCPG = 3785.4×FFC×FDEN

*Where: FFC = Fuel Fraction Carbon
FDEN = Fuel Density, g/mℓ

Note: GCPG is equal to 2421 for certification gasoline and 2778 for certification diesel fuel.

(1) OMFC multiplied by OM (in grams/mile as obtained in paragraph (c)).

(2) 0.429 multiplied by CO (in grams/mile as obtained in paragraph (c)), and

(3) 0.273 multiplied by CO_2 (in grams/mile as obtained in paragraph (c)).

*Where: OMFC is the fraction carbon in the exhaust organic matter. [If OM_C by FID divided by (CO_{2C} + CO_C) is less than 0.02, the FID measured value can generally be used for OM_C. Also, it can be assumed that OMFC = FFC].

Round the quotient to the nearest 0.1 mile per gallon.

<u>The following is based on Appendix II - Sample Test Value Calculation</u>

(a) Assume that a gasoline-fueled vehicle was tested by the Federal Emission Test Procedure and the following results were calculated:

HC = 1.03 grams/mile
CO = 6.74 grams/mile
CO_2 = 785 grams/mile

According to the preceding procedure, the fuel economy or MPG_C for the vehicle may be calculated by substituting the HC, CO and CO_2 grams/mile values into the following equation.

MPG_C = GCPG/(HCFC×HC + (0.429×CO) + (0.273×CO_2))

*For Certification Gasoline: FFC = 0.8656; FDEN = 0.739 g/mℓ

GCPG = 3785.4×0.8656×0.739 = 2421
HCFC = FFC = 0.8656 (or 0.866)*

MPG_C = 2421/((0.866×1.03) + (0.429×6.74) + (0.273×785)
= 2421/218.1 = 11.1 MPG

(b) Assume that the same vehicle was tested by the Federal Highway Fuel Economy Test Procedure and a calculation similar to that shown in (a) resulted in a highway fuel economy of MPG_h of 18.6. According to the procedure in §600.113, the combined fuel economy (called $MPG_{c/h}$) for the vehicle may be calculated by substituting the city and highway fuel economy values into the following equation:

$$MPG_{c/h} = 1/(0.55/MPG_c + 0.45/MPG_h)$$
$$= 1/(0.55/11.1 + 0.45/18.6) =$$
$$MPG_{c/h} = 13.6 \text{ MPG}$$

*(c) Assume that a methanol-fueled vehicle was tested and the same emission results were obtained (OM = 1.03 grams/mile).

Then: FFC = 0.375
FDEN = 0.7914 g/mℓ

GCPG = 3785.4×0.375×0.7914 = 1123
OMFC = FFC = 0.375

MPG = 1123/((0.375×1.03) + (0.429×6.74) + (0.273×785)
= 1123/217.6 = 5.2 MPG*

B. Fuel Economy Related Considerations

There are several potentially important additional fuel economy related considerations.

Energy Based Fuel Consumption - Alternate fuels can have a greatly different energy content per unit of volume and weight than is contained in current petroleum fuels. Therefore, fuel economy (or consumption) expressed only in miles per gallon (ℓ/100 km) can present a distorted picture of the actual fuel energy consumed. Fuel consumption expressed in terms of Btu per mile (J/km) can provide potentially useful information regarding the actual fuel energy consumed. Therefore, it is recommended that fuel consumption be expressed in Btu per mile, in addition to expressing fuel economy in miles per gallon. The calculation for energy based fuel consumption, derived in Appendix C-1, is as follows:

$$EBFC = 8.34 \times LHV \times FDEN/FE$$

Where:
EBFC = Energy Based Fuel Consumption, Btu/mi
LHV = Fuel Lower Heating Value, Btu/lb
FEDN = Fuel Density, g/mℓ
FE = Fuel Economy, mpg

Effect of Particulate Emissions - The fuel economy calculation in Subpart B does not account for the carbon in the particulate emissions. With a standard hydrocarbon diesel fuel and particulate emissions below 0.6 g/mi, the effect of the particulate emissions on the calculated fuel economy is considered to be negligible.

The effect of the particulate emissions on the calculated fuel economy can be determined as follows:

$$MPG_w = MPG/(1 + 0.00036 \times Part. \times PFC \times MPG)$$

Where:

- MPG_w = Calculated miles per gallon with particulate emissions included
- MPG = Calculated miles per gallon using the method in §600.113-78
- Part. = Particulate emissions rate in g/km
- PFC = Mass fraction of carbon in the particulate

Example values are given as follows:

Particulate Emissions, g/mi	Calculated Fuel Economy, mpg	
	MPG	MPG_w
0.2	25	24.9
0.2	50	49.8
0.6	25	24.8
0.6	50	49.5

For alternate fuels, the expression of fuel economy in terms of distance traveled per unit volume of fuel used may not always be sufficient to enable making meaningful comparisons.

Other Considerations - For additional discussion of methods for expressing fuel economy, the reader is referred to Reference 2.

VI. EVAPORATIVE EMISSIONS

Calculation of a mass value for evaporative emissions requires knowing the molecular weight per carbon atom of the emissions. The calculation method given in the light-duty certification procedure uses molecular weights derived from empirical data.[1] Those molecular weights, however, are only applicable to gasolines meeting the prescribed fuel specifications. Therefore, for alternate fuels, molecular weights have to be determined or satisfactorily estimated. Derivations of equations are given in Appendix C-2.

A. Evaporative HC Composition for Hydrocarbon Fuels

Detailed analyses for the composition of the evaporative hydrocarbon emissions is extremely difficult, and is considered to be an impractical requirement in the routine determination of evaporative emissions for experimental blends of hydrocarbon fuels. Therefore, assumption and methods for estimation of the composition of the evaporative HC emissions are given for various categories of such fuels as follows:

Standard Cuts of Hydrocarbon Fuels - Standard fuel cuts, containing hydrocarbons composed of carbon and hydrogen (at least ninety-nine percent) and providing for acceptable vehicle performance, would be expected to have reasonably similar distribution of hydrocarbon types regardless of the basic source of the fuel. For such fuels, the value of the molecular weight can be assumed to be the same value as used for certification gasoline.

Nonstandard Cuts or Blends of Hydrocarbon Fuels - For blends of individual hydrocarbons, these components could be analyzed for in the evaporative emissions using GC. For nonstandard cuts and for unknown blends, however, it will generally be necessary to estimate the composition of the evaporative emissions.

The extremes of the hydrogen-to-carbon ratios for hydrocarbons, that could be in gasoline or otherwise used as fuel, range from 1:1 (benzene) to 4:1 (methane). This results in extremes in the K value of 2.7 and 3.3. (The K value is equal to 0.208 times the molecular weight per carbon atom of the fuel and is used in the calculation of evaporative emissions. With the K value approaching 3.3, it is likely that the constituents would be known or could be readily determined. In all likelihood, the K value for a liquid hydrocarbon fuel consisting of essentially all carbon and hydrogen would be equal to or only slightly lower than 3.0. Therefore, for all liquid hydrocarbon fuels for use in gasoline engines, it is recommended that the K values for certification gasoline be used. For gaseous hydrocarbon fuels, it is recommended that the K value be determined using GC analyses of the evaporative hydrocarbon emissions (as an alternative a K value derived from the fuel constituent having the highest H/C ratio could be used).

B. Evaporative Organic Matter Composition for Other Fuels

The only method found to be generally acceptable for determination of evaporative organic matter composition with alternate fuels is to measure the individual evaporative components. The evaporative emissions should then be computed and reported separately for each of the major components.

C. Calculation of Evaporative Emissions

The following calculations for evaporative emissions are recommended for use when nonstandard carbon containing fuels are utilized. These calculations are based on the method given in 40 CFR Part 86, Subpart B, §86.143-78, with latest revisions incorporated. The basic format used in §86.143 has been retained. Changes or additions to the calculation method in §86.143-78 are identified by asterisk(8).

The following is based on §86.143-78 Calculations; evaporative emissions.

The calculation of the net hydrocarbon mass change in the enclosure is used to determine the diurnal and hot soak mass emissions. The mass is calculated using initial and final hydrocarbon concentrations in ppm carbon, initial and final enclosure ambient temperatures, initial and final barometric pressures, and net enclosure volume using the following equation:

$$C_{OM} = kV_n \times 10^{-4} \left[\frac{C_{OMf} P_{Bf}}{T_f} - \frac{C_{OMi} P_{Bi}}{T_i} \right]$$

Where:

M_{OM} = organic matter mass, g
C_{OM} = organic matter concentration as ppm carbon
V_n = net enclosure volume, ft^3(m^3) as determined by subtracting 50 ft^3 (1.42 m^3) or an approved measured volume, (volume of vehicle with trunk and windows open) from the enclosure volume.
P_B = barometric pressure, in Hg (kPa)
T = enclosure ambient temperature, R(K)
i = indicates initial reading
f = indicates final reading.

K = 0.208×(Mol. Wt. per carbon atom)
for SI units, K = 1.2×(Mol. Wt. per C)

For Certification Gasoline:

K = 2.98(17.2) for diurnal emissions, (MW/C = 14.33)
K = 2.95(17.0) for hot soak emissions, (MW/C = 14.18)

*For Other Fuels:

Molecular Weight per carbon atom is to be determined.*

The reported results shall be computed by summing the individual evaporative emission results determined in the diurnal breathing-loss test, the running-loss test, and the hot-soak test.

REFERENCES

1. Code of Federal Regulations, Title 40, Chapter 1, Part 86, Subpart B.

2. Harvey, Craig A., "Gasoline-Equivalent Fuel Economy Determined for Alternate Automotive Fuels," SAE Paper 820794, 1982.

3. Dietzmann, Harry E., et al, "Analytical Procedures for Characterizing Unregulated Pollutant Emissions from Motor Vehicles," Final Report EPA 600/2-79-017, February 1979.

4. Methane Measurement Using Gas Chromatography, SAE J1151a, Published in the 1980 SAE Handbook.

5. Smith, Lawrence R. and Urban, Charles, "Characterization of Exhaust Emissions from Methanol and Gasoline Fueled Automobiles," Final Report EPA 460/3-82-004, March 1982.

6. Bykowski, Bruce B., "Gasohol, TBA, MTBE Effects on Light-Duty Emissions," Final Report of Task No. 6 of EPA Contract 68-03-2377, October 1979.

7. Dietzmann, Harry E., et al, "Analytical Procedures for Characterizing Unregulated Pollutant Emissions from Vehicles Using Middle-Distillate Fuels," Interim Report EPA-600/2-80-068, April 1980.

8. Tejada, Silvestre B., et al, "Analysis of Nitroaromatics in Diesel and Gasoline Emissions," SAE Paper 820775.

9. Ames, B., et al, "Methods for Detecting Carcinogens and Mutagens with the Salmonella/Mannalian-Microsome Mutagenicity Test." Mutation Research, 31, pp, 347-364, 1975.

10. Code of Federal Regulations, Title 40, Chapter 1, Part 600, Subpart B.

11. Weast, Robert C., Ph.D., "Handbook of Chemistry and Physics," 54th Edition, CRC Press, 1974.

SELECTED BIBLIOGRAPHY

A number of other sources of information, although not directly utilized in this report, had an influence on the selection of the specific methods recommended and on the comments provided in this report.

Furey, Robert L., and King, Jack B., "Evaporative and Exhaust Emissions from Cars Fueled with Gasoline Containing Ethanol or Methyl tert-Butyl Ether," SAE Paper 800261.

Espinola, Stephen A., and Pefley, Richard K., "Alternate Fuel Influences on Emissions Test Procedures," Paper to be presented at the American Chemical Society Symposium on "Chemistry of Oxygenates in Fuel," September 12-17, 1982.

Wagner, T. O., et al. "Practicality of Alcohols as Motor Fuels," SAE Paper 790429.

Lawrence, D.C., and Niemczak, D.J., "Evaporative and Exhaust Emissions of Two Automobiles Fueled with Volatility Adjusted Gasohol," Paper EPA-AA-TED-81-12, December 1980.

Lang, J. M., and Black, F. M., "Impact of Gasohol on Automobile Evaporative and Tailpipe Emissions," SAE Paper 810438.

Dimitriades, B., and Joshi, S. B., "Application of Reactivity Criteria in Oxidant-Related Emission Control in the USA," International Conference Report EPA 600/3-77-001b, January 1977.

Memorandum from Frank Black, Chief, ETCS to Karl Hellman, Chief, CTAB, "Emissions and Fuel Consumption Measurements with Alternate Fuels," September 24, 1981.

Lawrence, Richard, "Fuel Economy Measurement Carbon Balance Method," Draft Report, October 1981.

California Air Resources Board, "Alcohol Fueled Fleet Test Program," Project 3T8001, Second Interim Report, July 1981.

Alson, Jeff, "A Brief Summary of the Technical Feasibility, Emissions and Fuel Ecnoomy of Pure Methanol Engines," Technical Report EPA-AA-SDSB-82-1, December 1981.

California Air Resources Board, "Fuel Economy Calculations for LPG Based on the Cold Start CVS-1975 Federal Test Procedure," Proposed amendments transmitted by letter dated August 3, 1982.

California Air Resources Board, "California Exhaust Standards and Test Procedures for Systems Designed to Convert Motor Vehicles to Use Alcohol or Alcohol/Gasoline Fuels," Proposed procedure received in September 1982.

APPENDICES

A. APPENDICES FOR SECTIONS I THROUGH III

B. APPENDICES FOR SECTION IV

C. APPENDICES FOR SECTIONS V AND VI

NOTE: The format used for mathematical equations is in accordance with that used in the Code of Federal Regulations.[1] Computations are to be performed in accordance with the IBM hierarchy of operations.

APPENDIX A

A-1. CVS FLOWRATE DETERMINATION
A-2. DERIVATION OF CO_2 CONCENTRATION ESTIMATION
A-3. DETERMINATION OF FID RESPONSE FACTOR
A-4. MEASUREMENT OF ALDEHYDES AND KETONES
A-5. MEASUREMENT OF METHANOL
A-6. MEASUREMENT OF ETHANOL

APPENDIX A-1

CVS FLOWRATE DETERMINATION

System H_2O Capacity = CVSFR×DEN_{AIR}×(SatSH - TestSH), wt/time

Where:

CVSFR = CVS flowrate, scfm
DEN_{AIR} = Density of air = 0.075 lb/scf
SatSH = Saturation specific humidity, lb/lb
TestSH = Specific humidity at test conditions, lb/lb

Fuel H_2O Addition = FC×FFH×18.016/2.016, wt/time

Where:

FC = Fuel Consumption in lb/min
= 1/MPG×Avg.MPH/60×8.34×FDEN
FFH = Fuel fraction hydrogen
MPG&MPH = Mile per gallon and per hour
FDEN = Density of the fuel, g/mℓ

Then:

CVSFR×0.075(SSH - TSH) = AMPH/MPG×FDEN×FFH×1.24
CVSFR = 16.56×AMPH×FDEN×FFN/(MPG (SSH - TSH))

APPENDIX A-2

DERIVATION OF CO_2 CONCENTRATION ESTIMATION

$$CO_2\% = (MRCO_2/MRAIR)\times(MWAIR/MWCO_2)\times 100$$

Where:

$MRCO_2$ = Mass flowrate of CO_2
= $1/FE\times AMPH\times 8.34\times FDEN\times(44.011/12.011)/60$
= $0.14\times AMPH\times FDEN/FE$

Where: FE = Fuel economy, mpg
AMPH = Average speed for the test cycle, mph
FDEN = fuel density, g/mℓ

MRAIR = $0.075\times CVSFR$

Where: CVSFR = flowrate of the CVS, scfm

MWAIR = 28.966
$MWCO_2$ = 44.011

$CO_2\% = (0.514\times AMPH\times FDEN/FE)/(0.075\times CVSFR)\times(28.966\times 44.011)\times 100$
$= (451\times AMPH\times FDEN)/(FE\times CVSFR)$

APPENDIX A-3

DETERMINATION OF FID RESPONSE FACTOR

For determination of the response factor of a specific FID hydrocarbon analyzer, with a liquid fuel, a standard of known concentration is prepared using the apparatus shown in Figure A-1. (Figure A-1 was adapted from SAE Paper 810438).

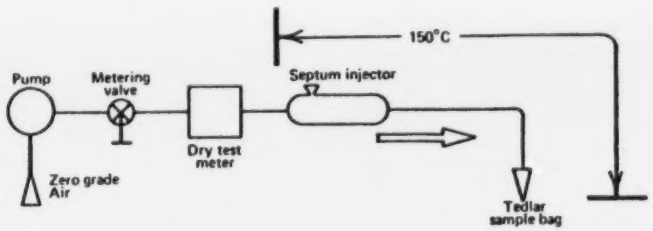


Figure 1. Apparatus for preparation of calibration mix

In preparing this standard, a known volume of the fuel of interest is injected, using a microliter syringe, into the heated mixing zone (150°C) of the apparatus. The liquids are vaporized and swept into a Tedlar bag with a known volume of air measured by a dry test meter. The concentration of the fuel (in ppm C) in the bag is determined as follows:

FCONC = FINJ×FDEN/AIRV×1000

Where:

FCONC = Concentration of the fuel, $\mu g/m^3$
FINJ = Volume of fuel injected, $\mu\ell$
FDEN = Density of the fuel, $g/m\ell$
AIRV = Volume of air, m^3 (scfm×0.02832)

FPPMC = FCONC×0.02406/FMWC

Where:

FPPMC = Fuel concentration as ppmC
0.02406 = Volume in m^3 of one mole at 29.92 in. Hg and 68°F
FMWC = Fuel molecular weight per carbon atom

Note: It is recommended that the response factor of the FID analyzer be determined at several concentrations in the range of the concentrations in the exhaust samples.

For gaseous fuels, the standards can be prepared using a precision proportioning system or any other available method that provides accurate volume measurements of the blending gases. For gaseous fuels:

$$GFPPMC = GFVOL \times CPM / (AIRV + GFVOL) \times 10^6$$

Where:

GFPPMC = ppmC of the gaseous fuel
GFVOL = Volume of the gaseous fuel
AIRV = Volume of air
CPM = Carbon atoms per molecule

The calibration sample is evaluated using the FID analyzer and the FID response factor is determined as follows:

$$FIDRF = FIDPPM / FPPMC$$

Where:

FIDRF = Response factor for the FID
FIDPPM = ppmC value as read on the FID
FPPMC = Actual fuel concentration as ppmC

Example A. Assume a gasoline with a density of 0.739 g/mℓ and a fuel fraction carbon of 0.8656.

$FMWC = 1/0.8656 \times 12.011 = 13.86$

Let: FINJ = 1.00
AIRV = 1 scfm = 0.02832 m^3

Then: $FCONC = 1.00 \times 0.739 / 0.02832 \times 1000 = 26{,}095$
$FPPMC = 26{,}095 \times 0.02406 / 13.86 = 45.4$

Let: FIDPPM = 45.4

Then: $FIDRF = 45.4 / 45.4 = 1.00$

Example B. Assume methanol is used as the fuel.

FMWC = 32.04
FDEN = 0.7914 g/mℓ

Let: FINJ = 1.00 µℓ
AIRV = 1 scfm = 0.02832 m^3

Then: $FCONC = 1.00 \times 0.7914 / 0.02832 \times 1000 = 27{,}945$
$FPPMC = 27{,}945 \times 0.02406 / 32.04 = 21.0$

Let: FIDPPM = 17.4

Then: $FIDRF = 17.4 / 21.0 = 0.83$

APPENDIX A-4

MEASUREMENT OF ALDEHYDES AND KETONES

The measurement of aldehydes (formaldehyde, acetaldehyde, isobutyraldehyde, crotonaldehyde, hexanaldehyde, and benzaldehyde) and ketones (acetone and methylethylketone) in exhaust is accomplished by bubbling the exhaust through glass impingers containing 2,4 dinitrophenylhydrazine (DNPH) in dilute hydrochloric acid. The exhaust sample is collected continuously during the test cycle. The aldehydes and ketones (also known as carbonyl compounds) react with the DNPH to form their respective phenylhydrazone derivatives. These derivatives are insoluble or only slightly soluble in the DNPH/HCl solution and are removed by filtration followed by pentane extractions. The filtered percipitate and the pentane extracts are combined and then the pentane is evaporated in a vacuum oven. The remaining dried extract contains the phenylhydrazone derivatives. The extract is dissolved in a quantitative volume of toluene containing a known amount of anthracene as an internal standard. A portion of this dissolved extract is injected into a gas chromatograph and analyzed using a flame ionization detector. The detection limits for this procedure under normal operating conditions are on the order of 0.005 ppm carbonyl compound in dilute exhaust.

LIST OF EQUIPMENT

The equipment required for the analysis of aldehydes and ketones is divided into three groups: sample acquisition, sample preparation, and sample analysis. Manufacturer, stock number and any pertinent descriptive information are listed.

Sample Acquisition

1. Glass impingers, Ace Glass Products, Catalog #7530-11, plain tapered tip stoppers with 18/7 arm joints and 29/42 bottle joints.

2. Flowmeter, Brooks Instrument Division, Model 1555, tube size R-2-15-C, graduated 0-15, sapphire float, 0-5 ℓ/min range.

3. Sample pump, Thomas Model 106 CA18, capable of free flow capacity of 4 ℓ/min.

4. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity.

5. Regulating valve, Nupro 4MG, stainless steel.

6. Teflon tubing, United States Plastic Corporation, 1/4" OD × 1/8" ID and 5/16" OD × 1/8" ID.

7. Teflon solenoid valve, The Fluorocarbon Company, Model DV2-144NCA1.

8. Drying tube, Analabs, Inc., Catalog #HGC-146, 6" long, 1/4" brass fittings.

9. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps, connectors, etc.

10. Digital readout for dry gas meter.

11. Miscellaneous electrical switches, lights, wirings, etc.

12. Six channel digital thermometer, Analog Devices, Model #2036/J/1.

13. Iron/Constantan type J single thermocouple with 1/4" OD stainless steel metal sheath, Thermo Sensors Corporation.

14. Variable autotransformer, Staco Inc., Type 3PN 1010.

15. Heating sleeve wrapped with insulation and insulation tape.

16. Class A, 20 mℓ volumetric pipets.

17. Class A, 1000 mℓ volumetric flask.

18. Teflon coated stirring bar.

19. Hot plate-stirrer, Corning, PC-351.

Sample Analysis

1. Varian 1700 gas chromatograph equipped with dual flame ionization detectors in differential operation, and a linear temperature programmer.

2. Soltec Model B-281 1 mv recorder.

3. Hewlett-Packard Model 3354 gas chromatograph computer system with remote teletype printout.

4. Syringe, 10 mℓ, Hamilton Company, #701.

5. Dual columns, 24 × 1/8" OD, stainless tubing packed with 6.7 percent Dexsil 300 GC on Chromosorb G 60/80 mesh, DMCS treated and acid washed.

Sample Preparation

1. Fritted glass filters, Ace Glass Company, porosity D, ASTM 10 - 20 microns pore size, 24/40 ground glass joint, vacuum takeoff.

2. Constant temperature vacuum oven, National Appliance Company.

3. Pump for oven, Thomas Industries, Model 907CA18 2.

4. Flasks, 125 mℓ capacity, 24/40 ground glass joints.

5. Separatory funnels, 125 mℓ.

6. Separatory funnels, 250 mℓ.

7. Separatory funnel shaker, Burrell Corporation, Wrist-Action (R) type with appropriate funnel holders, Model 75.

8. Ring stands, labels, holders, tubing, vacuum tubing, fittings and clamps needed for equipment manipulation.

9. Wash bottles, 500 mℓ.

10. Graduated cylinders, 50 mℓ.

11. Vials, Kimble, 1/2 dram.

12. Vacuum pump, Sargent-Welch.

LIST OF REAGENTS

A list of the reagents used in the determination of the aldehydes and ketones in exhaust is provided along with chemical formula, molecular weight, purity, manufacturer, and catalog number.

1. Hydrochloric acid, HCl, 36.46 g/mole, concentrated (37%), analytical reagent, Mallinckrodt, Cat. #2612.

2. Pentane, C_5H_{12}, 72.15 g/mole, Distilled in glass (bp 35-37°C), Burdick and Jackson Laboratories, Inc.

3. 2,4 Dinithrophenylhydrazine (2,4-DNPH), $(NO_2)_2C_6H_3CH{=}N{-}NH_2$, 210.149 g/mole, Aldrich analyzed, Aldrich, Cat. #D19,930-3.

4. Sodium Bicarbonate, $NaHCO_3$, 84.00 g/mole, Mallinckrodt, Cat. #7412.

5. Anthracene, $C_{14}H_{10}$, 178.24 g/mole, K and K Laboratories, Cat. #10714.

6. Toluene, $C_6H_5CH_3$, 92.14 g/mole Baker Analyzed Reagent, Baker Cat. #3-9460.

7. Methylene Chloride, CH_2Cl_2, 84.93 g/mole, Reagent ACS, Eastman, Cat. #13022.

PREPARATION OF ABSORBING SOLUTION

To prepare the absorbing solution, 163 mℓ of concentrated HCl and 2.5 g of 2,4-DNPH crystals are added to a one liter volumetric flask containing about 500 mℓ of deionized water. The flask is diluted to mark and stirred for several hours at room temperature with an automatic stirrer/teflon coated stirring bar to dissolve the DNPH. Fresh absorbing solution is prepared daily as needed.

PREPARATION OF TOLUENE/ANTRACENE SOLUTION

Toluene containing approximately 0.05 mg anthracene per mℓ of toluene is used to dissolve the dried phenylhydrazone extracts. This solution is made by adding 100 mg of anthracene to a two liter volumetric flask and diluting to mark with toluene.

PREPARATION OF PHENYLHYDRAZONE DERIVATIVES

In order to obtain response factors for each of the phenylhydrazone derivatives to anthracene, pure derivatives were prepared from their respective aldehydes and ketones. These derivatives were made by adding each of the carbonyl compounds separately to a 2N HCl-DNPH solution. The resulting orange to red precipitates were filtered and dried. The derivatives were then recrystallized from hot absolute ethanal. The melting points for each of the derivatives were compared to literature values before use. A GC trace was also made on each of the derivatives to further check the purity.

PREPARATION OF STANDARD SOLUTION OF PHENYLHYDRAZONE DERIVATIVES AND ANTRACENE

A standard containing the phenylhydrazone derivatives and anthracene in toluene is prepared to obtain a response factor of each of the derivatives to anthracene. The solution is made by dissolving weighed amounts of anthracene and each of the derivatives in a quantitative volume of toluene. These solutions contain approximately 0.05 mg anthrancene per mℓ of toluene and approximately 0.2 mg of each derivative per mℓ of toluene.

SAMPLING SYSTEM

Two glass impingers in series, each containing 40 mℓ of 2N HCl-2,4 dinitrophenylhydrazine, are used to collect exhaust samples for the analysis of the aldehydes and ketones. A flow schematic of the sample collection system is shown in Figure 1. The two impingers together trap approximately 98 percent of the carbonyl compounds. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. The dry gas meter determines the total flow through the impinger during a given driving cycle. The sample pump is capable of pulling a flow rate of 4 ℓ/min. A drier is included to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter allows continuous monitoring of the sample flow to insure proper flow rates during the sampling. The Teflon line connecting the CVS and the solenoid valve is heated to ∿170°F in order to prevent water from condensing in the line. Several views of the sampling system are shown in Figure 2.

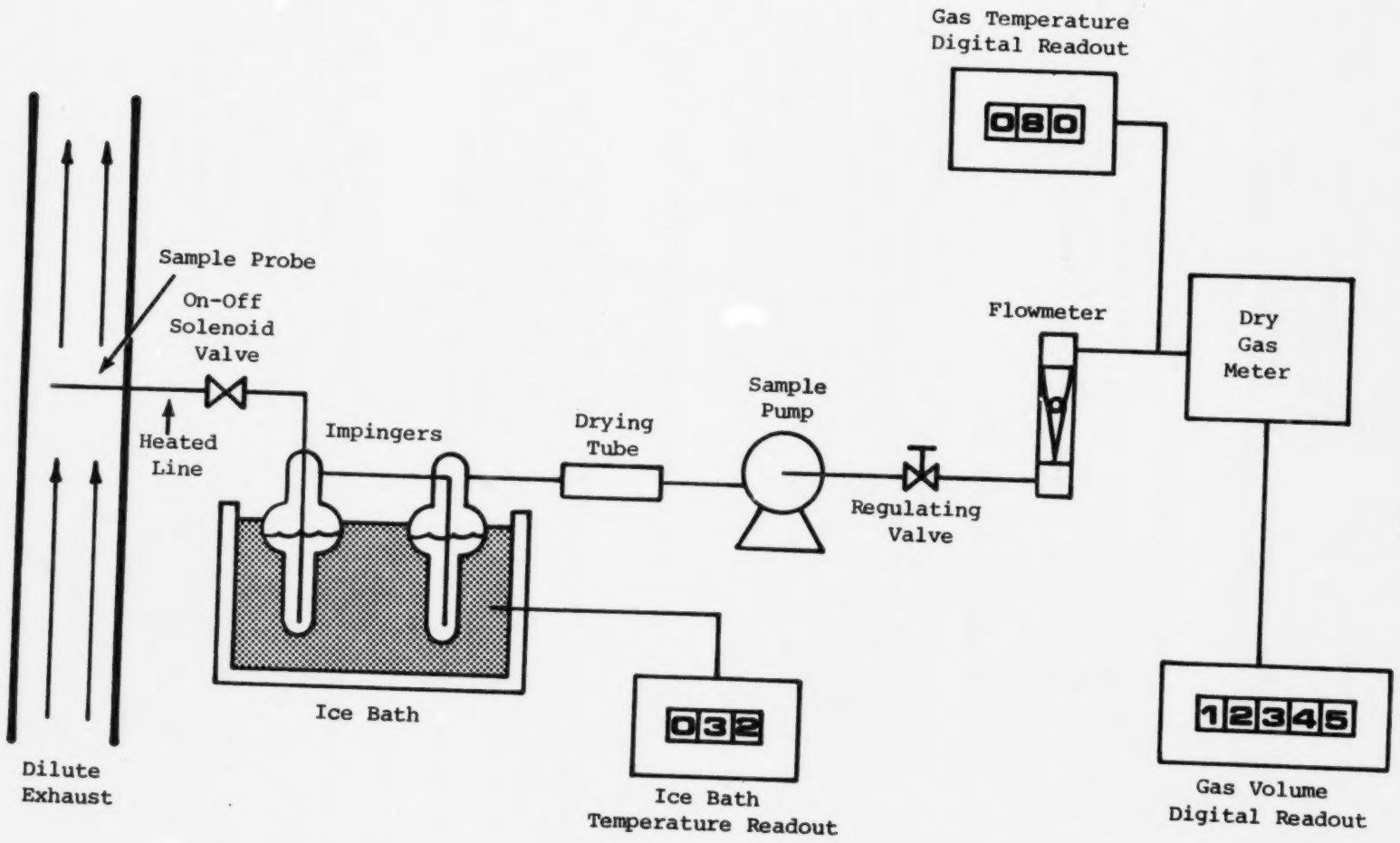
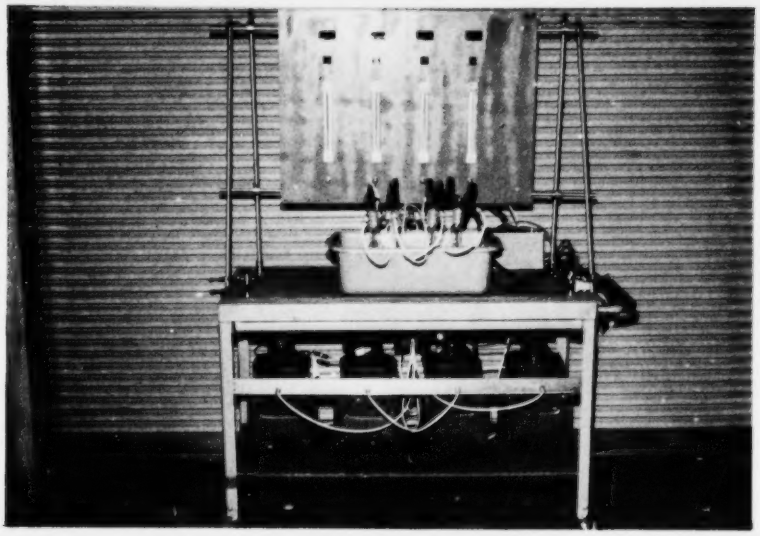
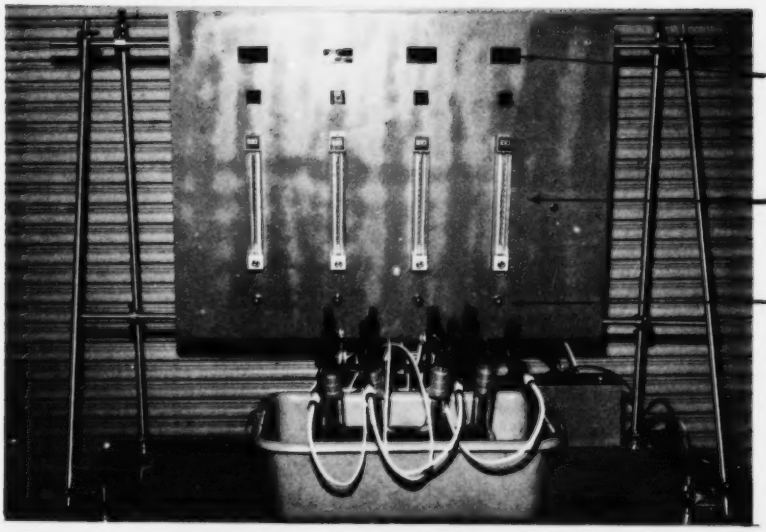


Figure 1. Aldehyde and Ketone sample collection flow schematic.

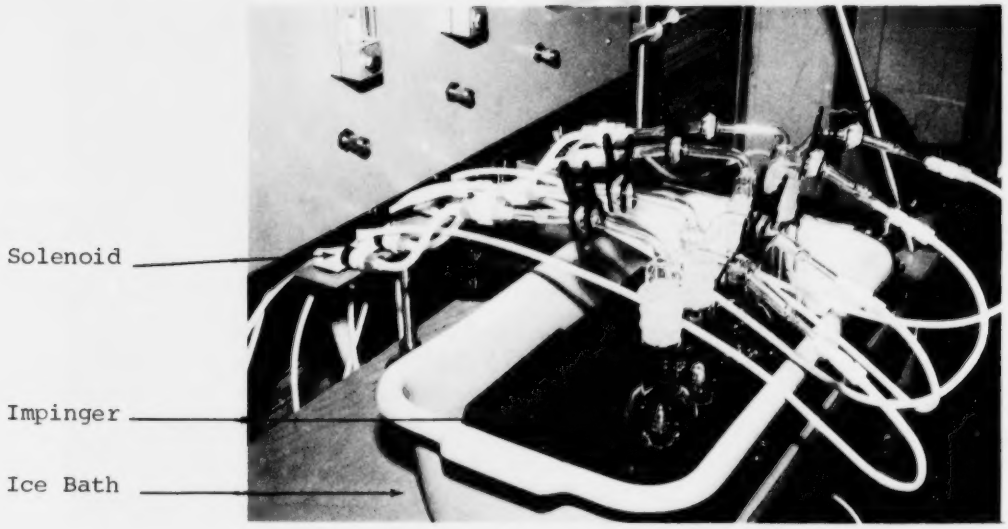


Front View

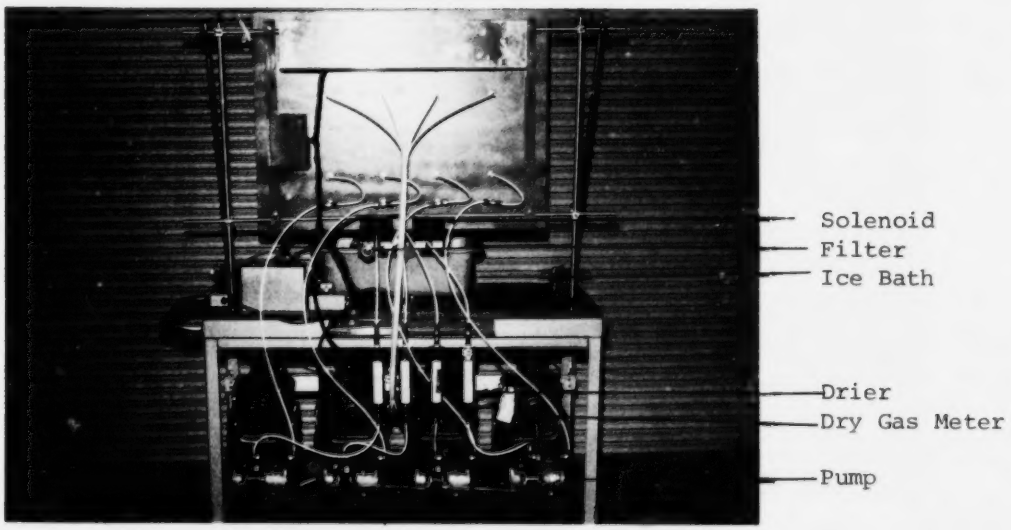


Close-Up of Upper Front

Figure 2. Aldehyde and Ketone sampling system.



Close-up of Impingers (Side View)



Rear View

Figure 2 (Cont'd). Methanol sampling system.

ANALYTICAL PROCEDURE

The analysis of the aldehydes (formaldehyde, acetaldehyde, isobutyraldehyde, crotonaldehyde, hexanaldehyde, and benzaldehyde) and of the ketones (acetone and methylethylketone) in dilute exhaust is accomplished by collecting these carbonyl compounds in a hydrochloric acid (HCl)/2,4 dinitrophenylhydrazine (DNPH) solution as their 2,4 dinitrophenylhydrazone derivatives. The derivatives are removed from the HCl/DNPH absorbing solution by filtration and/or extractions with pentane. The filtered precipitate and the pentane extracts are combined and the volatile solvents are removed. The remaining extract contains the phenylhydrazone derivatives. The derivatives are then dissolved in a quantitative volume of toluene containing a known amount of anthracene as an internal standard. This solution is analyzed by injecting a small volume of the solution into a gas chromatograph equipped with dual flame ionization detectors. From this analysis and the measured volume of exhaust sampled, the concentration of the carbonyl compounds in exhaust can be determined. The analysis flow schematic for the aldehydes and ketones is shown in Figure 3. A detailed description of the procedure follows.

The aldehydes and ketones are trapped in solution by bubbling a known volume of dilute exhaust through two glass impingers connected in series, with each impinger containing 40 mℓ of a 2N HCl solution saturated with DNPH. The sampling temperature and barometric pressure are recorded during this bubbling period. The carbonyl compounds in the exhaust react with the DNPH to form slightly soluble or insoluble 2,4 dinitrophenylhydrazone derivatives. The two impingers together collect 98 percent + of the carbonyls that are present in the exhaust. The impingers are removed from the sampling cart and are allowed to stand at room temperature for at least one hour before proceeding to the filtration and extraction steps. Figure 4 shows two impingers containing the HCl/DNPH absorbing solution after being removed from the sampling cart.

Under normal operating conditions the contents of the two impingers are combined and analyzed as one sample. If either of the two impingers contain a precipitate they are first subjected to a filtration step. If no percipitate is present this filtration step is omitted and the extraction step, described later in the procedure, is the first step.

For the filtration step the contents of the two impingers are poured through a fritted glass filter into a flask under vacuum (Figure 5). The two impingers are rinsed with small portions of deionized water. This wash water is also poured through the fritted glass filter. The precipitate in the filter is then washed with a few mℓ of deionized water. The fritted filter is then removed from the flask containing the 80 mℓ of absorbing reagent and the water washings. The flask is then set aside for the extraction step. The fritted glass filter containing the precipitate is connected to a dry flask. The two impingers that had previously contained the filtered precipitate are then each washed with small portions of methylene chloride. The methylene chloride dissolves any solid residue which was not removed by the water wash. These methylene chloride washings are poured into the fritted glass filter containing the precipitate. After

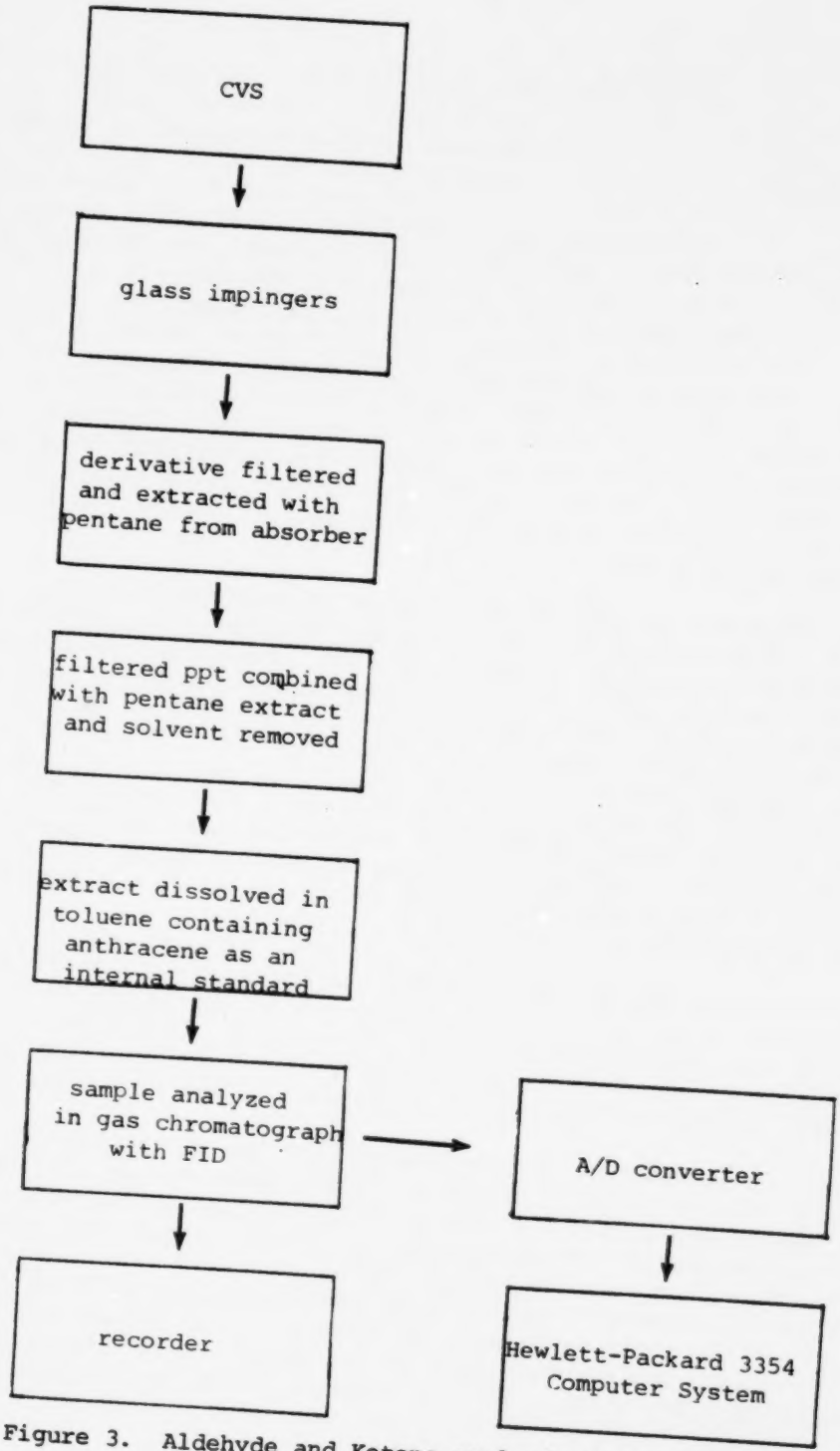

CVS
glass impingers
derivative filtered and extracted with pentane from absorber
filtered ppt combined with pentane extract and solvent removed
extract dissolved in toluene containing anthracene as an internal standard
sample analyzed in gas chromatograph with FID
A/D converter
recorder
Hewlett-Packard 3354 Computer System

Figure 3. Aldehyde and Ketone analysis flow schematic.

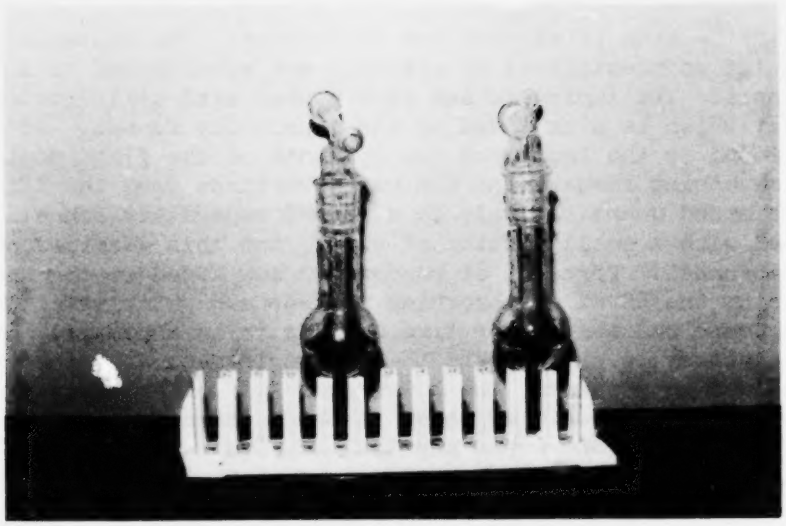


Figure 4. Impingers containing HCl/DNPH absorbing solution.

Figure 5. Filtration of absorbing solution.

the precipitate has been dissolved by the methylene chloride, a vacuum is applied to the flask and the methylene chloride solution is pulled through the filter into the flask. Another small amount of methylene chloride is poured through the filter into the flask to wash the filter. The methylene chloride solution is now saved until the extraction step is complete.

The extraction step is carried out as follows. The contents of the two impingers (if no precipitate is present) are transferred to a 250 mℓ separatory funnel. The impingers are each washed with small portions of deionized water which is also added to the separatory funnel. If a precipitate was found in the impingers the contents of the flask containing the filtered absorbing reagent and the water washings from the filtration step are transferred quantitatively to a 250 mℓ separatory funnel. The flask is washed with a small portion of water, and this water is added to the separatory funnel. Forty mℓ of pentane is now added to the separatory funnel containing the 80 mℓ of absorbing reagent and water washings. The funnel is stoppered and shaken for five minutes in an automatic shaker, Figure 6. The shaker is stopped and the funnel is vented. After the two phases are allowed to separate, the lower phase is collected in a second separatory funnel. The remaining phase is transferred to a third 250 mℓ separatory funnel. A second 40 mℓ portion of pentane is added to the already once extracted absorbing solution. The funnel is again stoppered, shaken for 5 minutes and vented. After the phases have separated the lower phase is again collected in another separatory funnel. The upper or pentane layer is combined with the pentane layer from the first extraction. A third 40 mℓ portion of pentane is added to the twice extracted absorbing solution and the extraction process repeated. After the third extraction the lower layer is discarded and the pentane layer is combined with the pentane layers from the first two extractions. Any absorbing solution which might have been accidently transferred with the pentane layers is drained off. Deionized water (25-50 mℓ) and sodium bicarbonate (1/4-1/2 gram) is added to the 250 mℓ separatory funnel containing the 120 mℓ of pentane extract. The funnel is stoppered and manually shaken for 30 seconds. The phases are allowed to separate and the lower water phase is drained off. Another 25 mℓ of deionized water is added and the shaking is repeated. After the phases have separated, the water is drained off insuring that all traces of water are removed. The contents of the funnel are then combined with the methylene chloride solution which was saved from the filtration step.

The flask containing the methylene chloride solution and the pentane extracts is then placed in a vacuum oven, Figure 7, operating at 50-60°C and 65" water vacuum until the pentane and methylene chloride have been removed. At this time only the dried phenylhydrazone derivatives remain.

Each time a series of samples are collected a blank containing 80 mℓ of HCl/DNPH solution is extracted and dried in the same manner as the samples. This accounts for any aldehydes or interfering compounds which might be found in the reagents used for extraction.

Two mℓ of toluene which contain a quantitative amount of anthracene (~0.05 mg/mℓ toluene) as an internal standard is pipetted into the flask

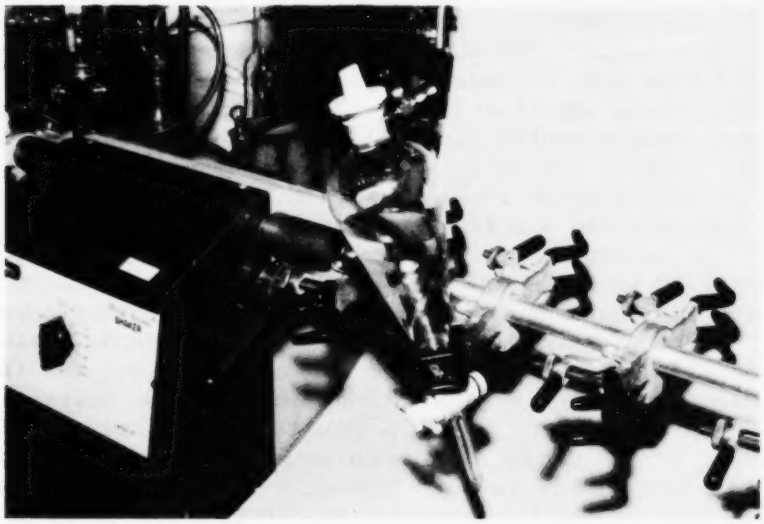


Figure 6. Automatic shaker.

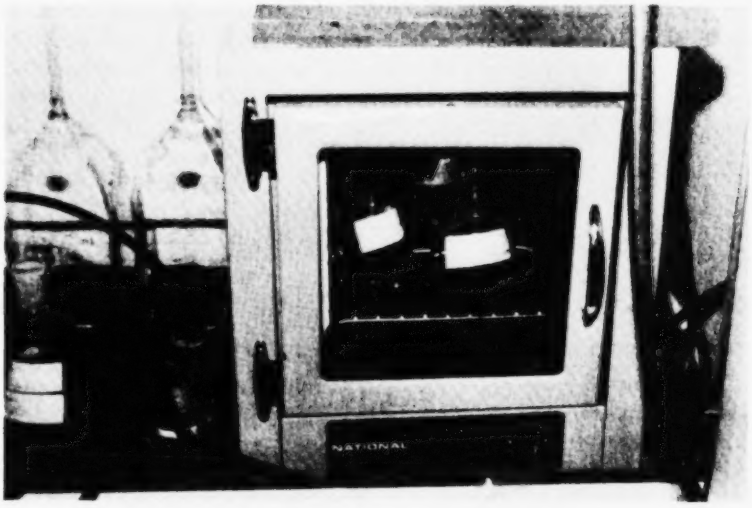


Figure 7. Vacuum oven.

containing the dried phenylhydrazone derivatives. The flask is then placed in a sonic bath until all of the residue is dissolved. After the precipitate has dissolved, the solution is transferred to a 1/2 dram vial. (See Figure 8.) At this point the derivative is ready for injection into the gas chromatograph system.

The gas chromatograph system used to analyze the toluene solution containing the phenylhydrazone derivatives is shown in Figure 9. The system consists of a Varian 1700 GC, an A/D converter, and a recorder. The GC is equipped with dual columns and dual flame ionization detectors with a single differential amplifier. The columns consist of 24 × 1/8 inch O.D. stainless steel tubing packed with 6.7 percent Dexsil (polycarboranesiloxane) 300 GC on DMCS treated and acid washed, 60/80 mesh Chromosorb G. The carrier gas is helium which flows through the columns at a rate of 40 mℓ/min. The optimum hydrogen and air flow rates are 500 mℓ/min and 35 mℓ/min respectively. The column temperature, after injection of the sample, is programmed from 120°C to 300°C at 8° a minute. In a chromatogram of a standard sample (Figure 10) containing anthracene and the phenylhydrazone derivatives of formaldehyde, acetaldehyde, acetone, iso-butyraldehyde, methylethylketone, crotonaldehyde, hexanaldehyde, and benzaldehyde, the first peak eluted is toluene followed by anthracene, and then the derivatives of formaldehyde, acetaldehyde, acetone, iso-butyraldehyde, methylethylketone, crotonaldehyde, hexanaldehyde and benyaldehyde. The methylethylketone derivative is added to the list of derivatives in order to name an unknown peak found in some of the exhaust samples. Data obtained from the five repetitive injections of the standard derivatives in toluene showed a maximum standard deviation of 4.56 percent for benzaldehyde and a minimum standard deviation of 0.87 percent for formaldehyde. The computer printout of the standard, Figure 10, is shown in Figure 11. This printout gives the retention time, area, and the name of each peak. The printout also gives the concentration of each of the derivatives in mg/mℓ. This concentration is calculated by the computer from response factors which are determined daily. Each day a standard containing known amounts of the derivatives and anthracene is injected into the GC. From the anthracene and derivative areas the computer calculates a response factor F. These F factors are used in all subsequent runs during the day to determine the concentration of the derivatives. This response is calculated from the following equation:

$$\text{Response Factor (F)} = \frac{\text{Anthracene Area}}{\text{Derivative Area}} \times \frac{\text{mg/mℓ Derivative}}{\text{mg/mℓ Anthracene}}$$

Typical response factors for each of the derivatives are listed below:

FACTOR	NAME
1.0000	ANTHRACENE
3.1043	FORMALDEHYDE
2.7736	ACETALDEHYDE
2.2366	ACETONE
2.4160	ISO-BUTYRALDEHYDE
2.3332	METHYLETHYLKETONE
3.4174	CROTONALDEHYDE

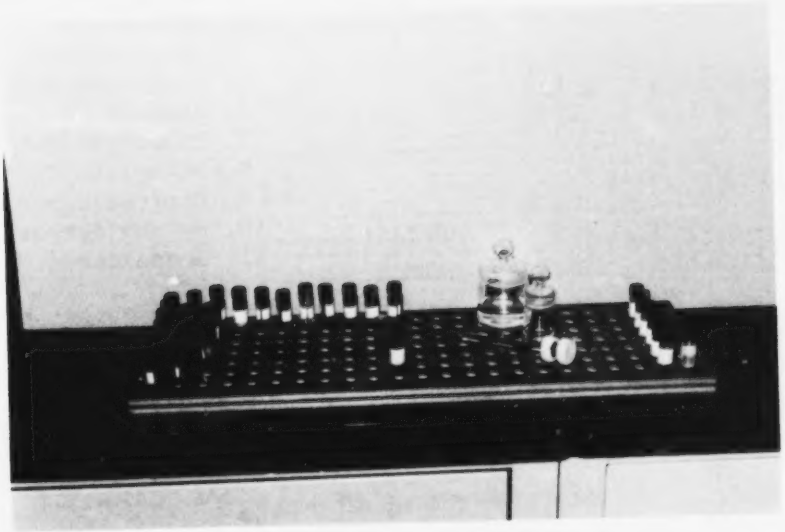


Figure 8. 1/2 dram vials.

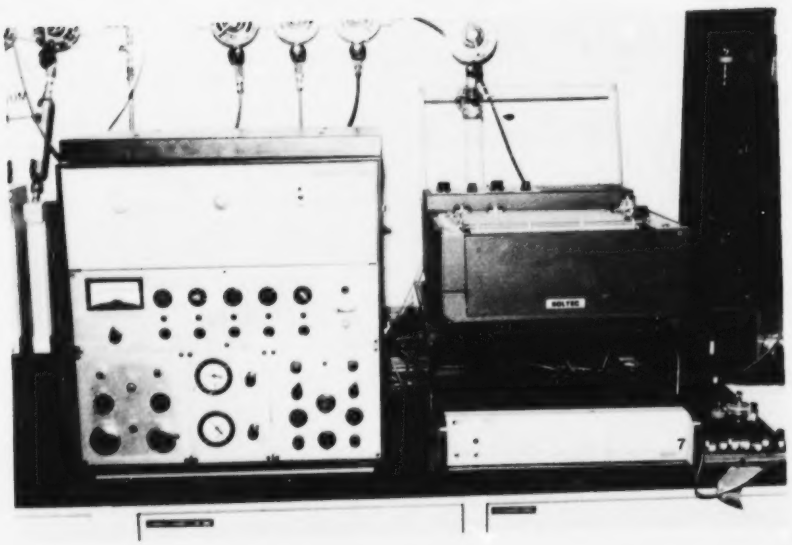


Figure 9. Aldehyde and ketone analytical system.

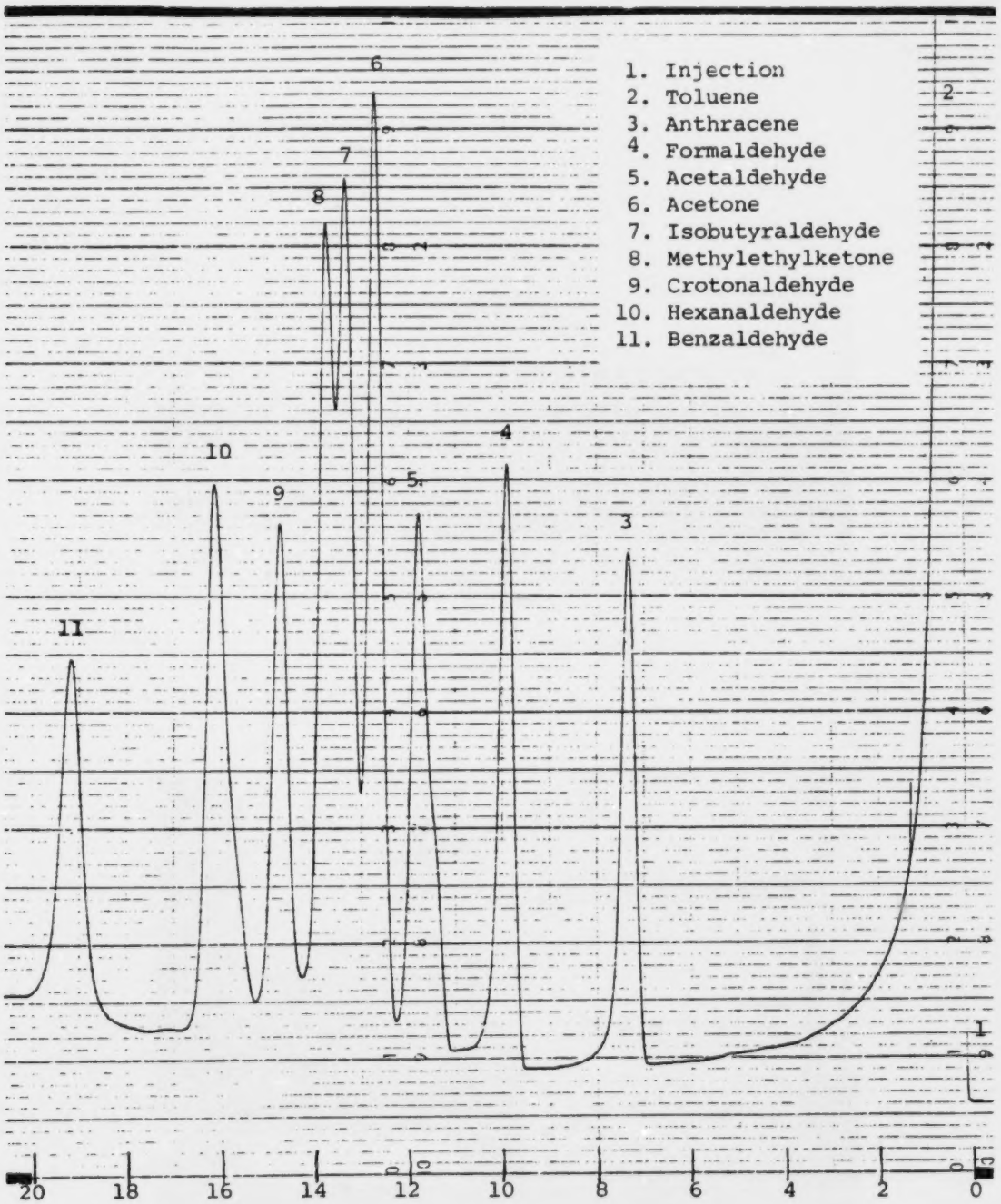


Figure 10. Chromatogram of standard.

REPORT: 14.11 CHANNEL: 11

SAMPLE: RCI INJECTED AT 11:18:27 ON MAR 1, 1978

ISTD METHOD: DNPH11

ACTUAL RUN TIME: 30.008 MINUTES

ISTD-RATIO: .050,R MG/ML STD-AMT: .0500 SAMP-AMT: 1.0000

ENDED NOT ON BL

RT	AREA		MG/ML	NAME
7.26	9638	BB		&ANTHRACENE
9.81	11159	BB	.190	#FORMALDEHYDE
11.71	13355	BV	.202	#ACETALDEHYDE
12.64	17898	VV	.211	#ACETONE
13.28	16448	VV	.213	#ISO-BUTYRALDEHYDE
13.70	16469	VV	.207	#MEK
14.69	11167	VV	.208	#CROTONALDEHYDE
16.08	15988	VV	.206	#HEXANALDEHYDE
17.08	74	VB	3.8E- 4	
19.08	10525	BB	.215	#BENZALDEHYDE
25.04	187	BB	9.7E- 4	

TOTAL AREA = 122909 TOTAL MG/ML = 1.650

Figure 11. Computer printout of standard.

2.3428	HEXANALDEHYDE
2.9329	BENZALDEHYDE

When the response factor is known a concentration in mg/mℓ for each of the derivatives can be found. This concentration, along with the volume of sampled exhaust is then used to calculate the concentration of the carbonyl compounds in exhaust. Figures 12 and 13 show a typical sample chromatogram and accompanying printout respectively.

CALCULATIONS

This procedure has been developed to provide the user with the concentrations of the aldehydes (formaldehyde, acetaldehyde, isobutyraldehyde, crotonaldehyde, hexanaldehyde, and benzaldehyde) and ketones (acetone and methylethylketone) in exhaust. The results will be expressed in $\mu g/m^3$ of exhaust and ppm for each carbonyl compound. The equations for determing the concentrations in $\mu g/m^3$ and ppm are derived in the following manner.

The first step is to correct the volume of exhaust sampled to a standard temperature, 68°F and pressure, 29.92" Hg, by use of the equation

$$\frac{P_{exp} \times V_{exp}}{T_{exp}} = \frac{P_{corr} \times V_{corr}}{T_{corr}}$$

V_{exp} = experimental volume of gas sampled in ft^3
V_{corr} = volume of gas sampled in ft^3 corrected to 68°F and 29.92" Hg
P_{exp} = experimental barometric pressure
P_{corr} = 29.92" Hg
T_{exp} = experimental temperature in °F + 460
T_{corr} = 68°F + 460 = 528°R

Solving for V_{corr} gives:

$$V_{corr} = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp}\ (°R) \quad 29.92\text{" Hg}}$$

The next step converts the volume from cubic feet to cubic meters by use of the conversion factor 1 cubic meter is equal to 35.31 cubic feet.

$$V_{corr(m^3)} = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°}{T_{exp} \times 29.92\text{" Hg} \times 35.31\ ft^3/m^3}$$

(Equation 1)

The next step converts the mg/mℓ of derivative determined by the computer to mg of carbonyl collected in the two impingers. To obtain mg of derivative, the concentration (from the computer printout) in mg/mℓ is multiplied by the volume of toluene used to dissolve the solid extract.

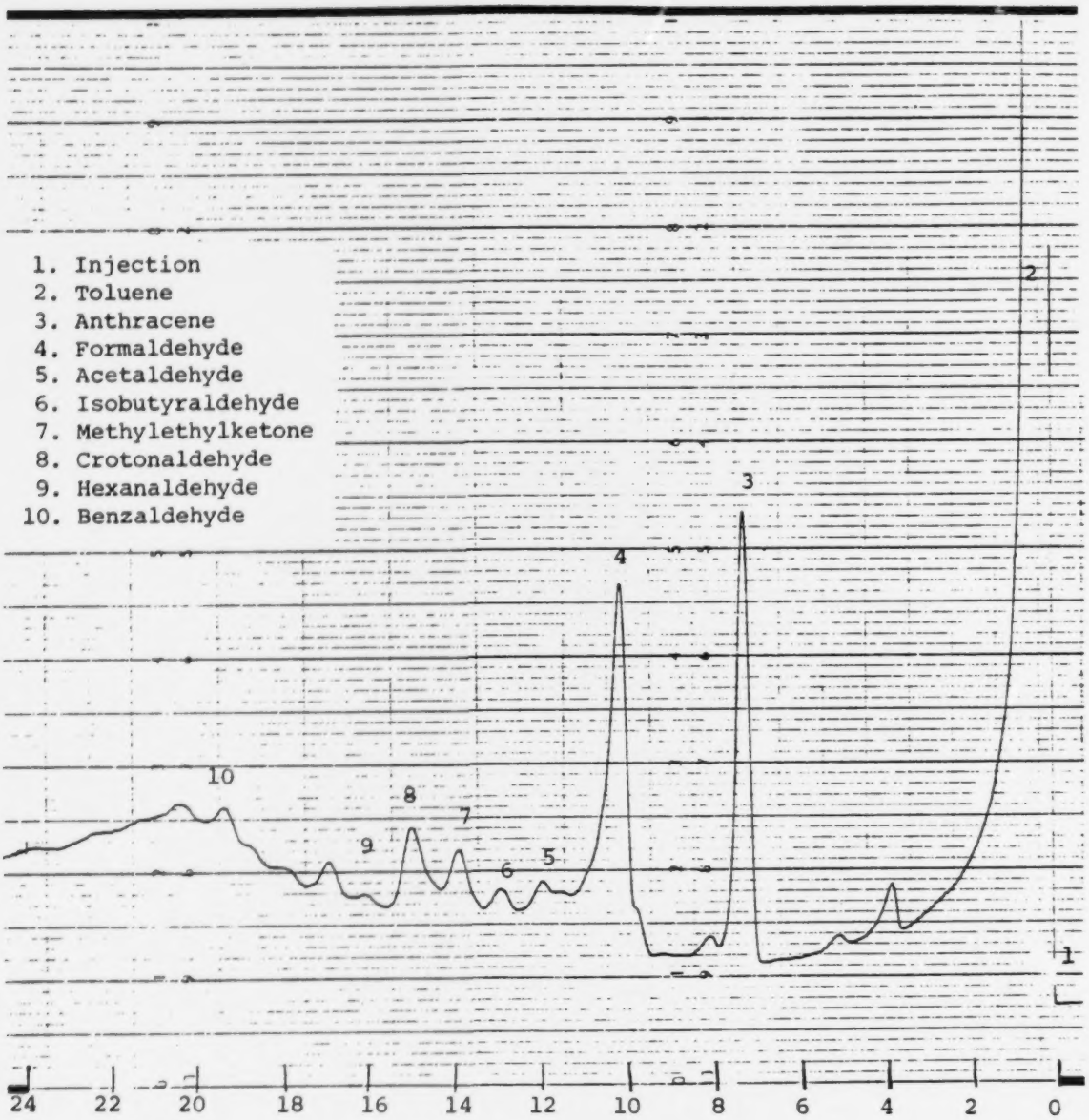


Figure 12. Sample chromatogram.

REPORT: 20 CHANNEL: 11

SAMPLE: RCI INJECTED AT 15:41:05 ON MAR 1, 1978

ISTD METHOD: DNPH11

ACTUAL RUN TIME: 30.017 MINUTES

ISTD-RATIO: .3508 MG/ML STD-AMT: .0500 SAMP-AMT: 1.0000

RT	AREA		MG/ML	NAME
7.15	8604	BV		#ANTHRACENE
7.95	435	VB	.003	
10.03	8877	BB	.186	#FORMALDEHYDE
11.88	575	BV	.010	#ACETALDEHYDE
12.83	463	VV	.007	#ISO-BUTYRALDEHYDE
13.78	1594	VV	.022	#MEK
14.85	2630	VV	.053	#CROTONALDEHYDE
15.95	146	VV	.002	#HEXANALDEHYDE
16.77	675	VV	.004	
19.20	648	VB	.012	#BENZALDEHYDE
20.23	1912	BV	.011	
23.52	217	VV	.001	
25.43	13	VB	7.6E- 5	
25.48	84	BB	4.9E- 4	

TOTAL AREA = 26874 TOTAL MG/ML = .310

PROCESSED DATA FILE: *PRC11 RAW DATA FILE: *RAW11

Figure 13. Computer printout of sample.

$$\text{mg derivative} = \text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell)$$

To find mg of carbonyl compound per sample the mg of derivative are multiplied by the ratio of the molecular weight of the carbonyl derivative over the molecular weight of its phenylhydrazone derivative.

$$\text{mg carbonyl} = \text{mg derivative} \times \frac{\text{mol. wt. carbonyl}}{\text{mol. wt. derivative}}$$

$$= \text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell) \times \frac{\text{mol. wt. carbonyl}}{\text{mol. wt. derivative}}$$

To obtain the number of µg of carbonyl compound the mg of carbonyl are multiplied by the conversion factor, 1000 µg/mg

$$\text{µg carbonyl} = \text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell) \times \frac{\text{Mol. Wt. carbonyl}}{\text{Mol. Wt. derivative}} \times 1000\ \text{µg/mg}$$

(Equation 2)

The concentration of the carbonyl compound in exhaust can now be found in µg/m^3 by dividing equation 2 by equation 1.

$$\text{µg carbonyl/m}^3 = \frac{\text{Conc}_{\text{Der}}\ (\text{mg/m}\ell) \times \text{Vol}_{\text{Tol}}\ (\text{m}\ell) \times \text{mol. wt. carbonyl}}{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (\text{ft}^3) \times 528^\circ} \times \frac{1000\ \text{µg/mg} \times T_{exp}\ (^\circ\text{R}) \times 29.29\text{" Hg} \times 35.31\ \text{ft}^3/\text{m}^3}{\text{mol. wt. derivative}}$$

(Equation 3)

To find the concentration of each carbonyl compound in ppm, the densities of carbonyls are needed. At 29.92" Hg and 32°F, one mole of gas occupies 22.4 liters. This volume is corrected to 68°F from the equation.

$$\frac{V}{T} = \frac{V_1}{T_1}$$

$V_1 = 22.4$
$T_1 = 32^\circ\text{F} + 460 = 492^\circ\text{R}$
V = volume at 68°F
$T = 68^\circ\text{F} + 460 = 528^\circ\text{R}$

Solving for V gives:

$$V = \frac{V_1 \times T}{T_1} = \frac{22.4 \times 528}{492} = 24.04\ell$$

Since one mole of gas occupies 22.04ℓ at 68°F, the denisty can be found in g/ℓ by dividing the molecular weight in g/mole by 24.04 ℓ/mole

$$\text{den (g/ℓ)} = \frac{\text{mol. wt. (g/mole)}}{24.04\text{ℓ/mole}}$$

The density in μg/mℓ can be found by converting g to μg and μg and ℓ to mℓ as follows:

$$\text{den } \mu g/m\ell = \frac{\text{mol. wt. g/mole}}{24.04\ell/\text{mole}} \times \frac{1 \times 10^6\ \mu g/g}{1 \times 10^3\ m\ell/\ell} \times \frac{\text{mol. wt.} \times 1000}{24.04}$$

(Equation 4)

To obtain the concentration of each carbonyl in ppm, the concentration in $\mu g/m^3$ is divided by the density in μg/mℓ

$$\text{ppm} = \mu g/m^3 \div \mu g/m\ell = \frac{m\ell}{m^3}$$

Using Equations 3 and 4 gives the ppm concentration in the form of the raw data.

$$\text{ppm} = \frac{\text{Conc}_{Der}\ (mg/m\ell) \times \text{Vol}_{Tol}\ (m\ell) \times \text{mol. wt. carbonyl} \times 1000\ \mu g/m\ell}{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528° \times \text{mol. wt. derivative}}$$

$$\times \frac{T_{exp}\ (°R) \times 29.92\text{" Hg} \times 35.31\ ft^3/m^3 \times 24.04\ \ell/\text{mole}}{\text{mol. wt. carbonyl} \times 1000}$$

$$= \frac{\text{Con}_{Der}\ (mg/m\ell) \times \text{Vol}_{Tol}\ (m\ell) \times T_{exp}\ (°R) \times 29.92\text{" Hg}}{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°}$$

$$\times \frac{35.35\ ft^3/m^3 \times 24.04\ \ell/\text{mole}}{\text{mol. wt. derivative}}$$

(Equation 5)

At this point, the concentration can be express in $\mu g/m^3$ (Equation 3) and ppm (Equation 5) at 68°F and 29.92" Hg from the raw data.

Hewlett-Packard Calculations

In order to insure maximum turnaround in a minimum time period, two Hewlett-Packard 65 programs were developed. One calculates the aldehyde and ketone concentrations in $\mu g/m^3$ from the raw data and phenylhydrazone derivative concentrations (from computer printout). The other program calculates the concentrations in ppm from the concentrations in $\mu g/m^3$. These programs are presented in Figures 14 and 15.

HP-65 Program Form

Title _____ Page ____ of ____

SWITCH TO W/PRGM PRESS f PRGM TO CLEAR MEMORY

KEY ENTRY	CODE SHOWN	COMMENTS
LBL	23	
A	11	Input sample vol., ft^3
0		
•	83	
0		
0		
0		
5		
X	71	
R/S	84	Input Barometer, "Hg
X	71	
STO1	3301	
R/S	84	Input sample Temp °F
4		
6		
0		
+	61	
RCL1	3401	
g x≷y	3507	
30 ÷	81	
g 1/x	3504	
R/S	84	Input Vol. Toluene, ml
X	71	
STO2	3302	
R/S	84	In mg/m.
RCL2	3402	
X	71	
0		
•	83	
01		
4		
3		
X	71	
R/S	84	Out $\mu g/m^3$; In mg/ml
RCL 2	3402	
X	71	
0		
•	83	
1		
9		
6		
X	71	
R/S	84	Out $\mu g/m^3$; In mg/ml
RCL 2	3402	
X	71	
0		
•	83	
2		
4		
4		

KEY ENTRY	CODE SHOWN	COMMENTS
X	71	
R/S	84	Out $\mu g/m^3$; In mg/ml
RCL2	3402	
X	71	
0		
•	83	
2		
8		
6		
X	71	
R/S	84	Out $\mu g/m^3$; In mg/ml
RCL2	3402	
X	71	
0		
•	83	
2		
8		
6		
X	71	
R/S	84	Out $\mu g/m^3$; In mg/ml
RCL2	3402	
X	71	
0		
•	83	
2		
8		
0		
X	71	
R/S	84	Out $\mu g/m^3$; In mg/ml
RCL2	3402	
X	71	
0		
•	83	
3		
5		
9		
X	71	
R/S	84	Out $\mu g/m^3$; In mg/ml
RCL2	3402	
X	71	
0		
•	83	
3		
7		
1		
X	71	
R/S	84	Out $\mu g/m^3$
RTN	24	

REGISTERS
R_1
R_2
R_3
R_4
R_5
R_6
R_7
R_8
R_9

LABELS
A
B
C
D
E
0
1
2
3
4
5
6
7
8
9

FLAGS
1
2

TO RECORD PROGRAM INSERT MAGNETIC CARD WITH SWITCH SET AT W PRGM

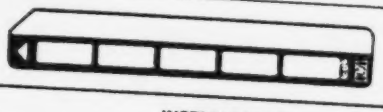
Figure 14. Aldehyde and Ketone concentrations in µg/mℓ.

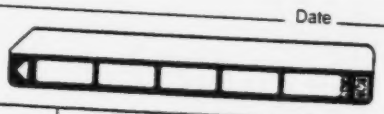
HP-65 User Instructions

Title _____

Programmer _____ Page ____ of ____

Date _____





STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS	OUTPUT DATA/UNITS
O_1	Switch to on; switch to run			
O_2	Feed card in from right to left			
O_3	Initialize		f REG	
O_4	Set decimal place		DSP 2	
1	Input - sample volume, ft^3		A	
2	Input - barometric pressure, "Hg		R/S	
3	Input - Sample Temperature, °F		R/S	
4	Input - Volume Tolune, ml		R/S	
5	Input - Conc. Formaldehyde Der, mg/ml		R/S	
	Output - Conc. Formaldehyde $\mu g/m^3$			
6	Input - Conc. Acetaldehyde Der, mg/ml		R/S	
	Output - Conc. Acetaldehyde $\mu g/m^3$			
7	Input - Conc. Acetone Der, mg/ml		R/S	
	Output - Conc. Acetone, $\mu g/m^3$			
8	Input - Conc. Isobutyraldehyde Der, mg/ml		R/S	
	Output - Conc. Isobutyraldehyde, $\mu g/m^3$			
9	Input - Conc. methylethylketone Der, mg/ml		R/S	
	Output - Conc. methylethylketone, $\mu g/m^3$			
10	Input - Conc. Crotonaldehyde Der, mg/ml		R/S	
	Output - Conc. Crotonaldehyde, $\mu g/m^3$			
11	Input - Conc. Hexanaldehyde Der, mg/ml		R/S	
	Output - Conc. Hexanaldehyde, $\mu g/m^3$			
12	Input - Conc. Benzaldehyde Der, mg/ml		R/S	
	Output - Conc. Benzaledhyde $\mu g/m^3$			
			RTN	
			f	

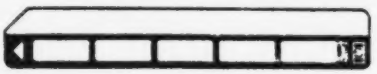
(cont'd.)

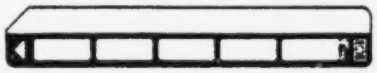
Figure 14 (Cont'd). Aldehyde and Ketone concentrations in µg/mℓ.

HP-65 User Instructions

Title _____ Page ____ of ____

Programmer _____ Date _____





STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS	OUTPUT DATA/UNITS
O_1	Switch to on; switch to run			
O_2	Feed card in from right to left			
O_3	Initialize		f REG	
O_4	Set decimal place		DSP 2	
1	Input-conc Formaldehyde, $\mu g/m^3$		A	
	Ouput-conc Formaldehyde, ppm			
2	Input-Conc Acetaldehyde, $\mu g/m^3$		R/S	
	Output-Conc Acetaldehyde, ppm			
3	Input-Conc Acetone, $\mu g/m^3$		R/S	
	Output-Conc Acetone, ppm			
4	Input-Conc Isobutyraldehyde, $\mu g/m^3$		R/S	
	Output-Conc Isobutyraldehyde, ppm			
5	Input-Conc Methylethylketone, $\mu g/m^3$		R/S	
	Output-Conc Methylethylketone, ppm			
6	Input-Conc Crotonaldehyde, $\mu g/m^3$		R/S	
	Output-Conc Crotonaldehyde, ppm			
7	Input-Conc Hexanaldehyde, $\mu g/m^3$		R/S	
	Output-Conc Hexanaldehyde, ppm			
8	Input-Conc Benzaldehyde, $\mu g/m^3$		R/S	
	Output-Conc Benzaldehyde, ppm			
			RTN	
			f	
			REG	
			CLX	

Figure 15. Aldehyde and Ketone concentrations in ppm.

HP-65 Program Form

Title _____ Page ____

SWITCH TO ▼ PRGM · PRESS ▽ PRGM · TO CLEAR MEMORY

KEY ENTRY	CODE SHOWN	COMMENTS
LBL	23	
A	11	In conc Lg/m^3
1		
2		
4		
9		
÷	81	
R/S	84	Out conc ppm
		In conc ug/m^3
1		
8		
3		
2		
÷	81	
R/S	84	Out conc ppm
		In conc ug/m^3
2		
1		
1		
6		
÷	81	
R/S	84	Out conc ppm
		In conc ug/m^3
3		
0		
0		
2		
÷	81	
R/S	84	Out conc ppm
		In conc ug/m^3
3		
0		
2		
0		
÷	81	
R/S	84	Out conc ppm
		In conc ug/m^3
2		
9		
5		
2		
÷	81	
R/S	84	Out conc ppm
		In conc ug/m^3
4		
1		
6		
6		
÷	81	
R/S	84	Out conc ppm

KEY ENTRY	CODE SHOWN	COMMENTS
		In conc Lg/m^3
4		
4		
1		
5		
÷	81	
R/S	84	Out conc ppm
RTN	24	

REGISTERS
R1
R2
R3
R4
R5
R6
R7
R8
R9

LABELS
A
B
C
D
E
0
1
2
3
4
5
6
7
8
9

FLAGS
1
2

TO RECORD PROGRAM INSERT MAGNETIC CARD WITH SWITCH SET AT ▼ PRGM

Figure 15 Cont'd. Aldehyde and Ketone concentrations in ppm.

Sample Calculation

Assume exhaust samples were collected in glass impingers for each portion of a three bag 1975 FTP. Raw data for these tests is presented in Figure 16. Calculations were performed using the HP-65 programs and manual calculations.

Manual calculation for driving cycle FTP-1:

$$\mu g/m^3 \text{ formaldehyde} = \frac{Conc_{Der}\ (mg/m\ell) \times Vol_{Tol}\ (m\ell) \times \text{mol. wt. carbonyl}}{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3)}$$

$$\times \frac{1000\ \mu g/mg \times T_{exp}\ (°R) \times 29.92\text{" Hg}}{528°R}$$

$$\times \frac{35.31\ ft^3/m^3}{\text{mol. wt. derivative}}$$

$$= \frac{0.186\ mg/m\ell \times 2m\ell \times 30.03\ g/mole \times 1000\ \mu g/mg}{29.80\text{" Hg} \times 3.196\ ft^3 \times 528°R}$$

$$\times \frac{535°R \times 29.92\text{" Hg} \times 35.31\ ft^3/m^3}{201.15\ g/mole}$$

$$= 597.5\ \mu g/m^3$$

$$\text{ppm formaldehyde} = \mu g/m^3 \div \text{density } \mu g/m\ell$$

$$\text{density } \mu g/m\ell = \frac{\text{mol. wt. (formaldehyde)} \times 1000}{24.04\ell}$$

$$\text{mol. wt. formaldehyde} = 30.03\ g/mole$$

$$\text{density} = \frac{30.03\ g/mole \times 1000}{24.04\ell} = 1249\ \mu g/m\ell$$

$$\text{ppm} = 597.5\ \mu g/m^3 \div 1249\ \mu g/m\ell = 0.478\ m\ell/m^3 = 0.478\ \text{ppm}$$

The calculations for acetaldehyde, acetone, isobutyraldehyde, methylethyketone, crotonaldehyde, hexanaldehyde, and benzaldehyde are carried out in the same manner by substituting the appropriate derivative concentrations and molecular weights into the above formulas. These calculations give the following concentrations:

acetaldehyde, 561 $\mu g/m^3$ and 0.306 ppm
acetone, 663 $\mu g/m^3$ and 0.274 ppm
isobutyraldehyde, 141 $\mu g/m^3$ and 0.047 ppm
methylethylketone, 630 $\mu g/m^3$ and 0.210 ppm
crotonaldehyde, 541 $\mu g/m^3$ and 0.186 ppm
hexanaldehyde, 250 $\mu g/m^3$ and 0.060 ppm

SWRI PROJECT NO._____TEST NO._____TEST DATE:_____VEHICLE:_____

FUEL:_____CVS NO._____TUNNEL SIZE:_____DRIVER:_____MILES:_____

SAMPLE COLLECTION BY:_____CHEMICAL ANALYSIS BY:_____CALCULATIONS BY:_____

GENERAL COMMENTS:_____

Test No.	1	2	3	4	5	6
Driving Cycle	FTP-1	FTP-2	FTP-3	SET-7	HFET	NYCC
Volume, Ft^3	3.196	1.625	2.010	3.730	8.241	1.070
B.P., "Hg	29.80	30.02	29.02	29.25	29.95	29.50
Temp. °F	75	80	96	85	83	89
Vol. Toluene ml	2	2	2	2	2	2
Formaldehyde Der Conc mg/ml	0.186	0.105	0.201	0.312	0.732	0.142
Formaldehyde Conc $\mu g/m^3$	598	665	1100	891	921	1410
Formaldehyde Conc ppm	0.479	0.532	0.881	0.713	0.737	1.130
Acetaldehyde Der Conc mg/ml	0.127	0.092	0.157	0.282	0.612	0.102
Acetaldehyde Conc $\mu g/m^3$	559	798	1170	1100	1060	1390
Acetaldehyde Conc ppm	0.305	0.436	0.639	0.600	0.579	0.759
Acetone Der Conc mg/ml	0.121	0.098	0.161	0.285	0.595	0.105
Acetone Conc $\mu g/m^3$	663	1060	1500	1390	1280	1780
Acetone Conc ppm	0.274	0.439	0.621	0.575	0.530	0.737
I-Bu Aldehyde Der Conc mg/ml	0.022	0.011	0.028	0.023	0.051	0.009
I-Bu Aldehyde Conc $\mu g/m^3$	141	139	305	131	128	179
I-Bu Aldehyde Conc ppm	0.047	0.046	0.102	0.044	0.043	0.060
MeEt Ketone Der Conc mg/ml	0.098	0.084	0.097	0.198	0.252	0.075
MeEt Ketone Conc $\mu g/m^3$	630	1060	1060	1130	634	1490
MeEt Ketone Conc ppm	0.210	0.353	0.353	0.377	0.211	0.497
Cro-Aldehyde Der Conc mg/ml	0.086	0.074	0.076	0.105	0.286	0.072
Cro-Aldehyde Conc $\mu g/m^3$	541	917	811	587	705	1400
Cro-Aldehyde Conc ppm	0.186	0.314	0.278	0.201	0.242	0.480
Hex-Aldehyde Der Conc mg/ml	0.031	0.018	0.030	0.027	0.078	0.011
Hex-Aldehyde Conc $\mu g/m^3$	250	286	411	194	246	275
Hex-Aldehyde Conc ppm	0.060	0.069	0.099	0.047	0.059	0.066
Benzaldehyde Der Conc mg/ml	0.093	0.081	0.097	0.121	0.232	0.081
Benzaldehyde Conc $\mu g/m^3$	775	1330	1370	897	757	2090
Benzaldehyde Conc ppm	0.176	0.301	0.310	0.203	0.171	0.473

Figure 16. Aldehyde Collection Sheet.

Benzaldehyde, 775 g/m^3 and 0.176 ppm.

Note: The values used in these calculations are picked from a range of temperatures, derivative concentrations, etc. to validate the calculations and may not be representative of expected raw data. The calculations are presented to confirm the manual and HP-65 calculations give the same results. This was confirmed for six sets of calculations.

REFERENCES

This procedure is taken from the procedure: "Oxygenated Compounds in Automobile Exhaust-Gas Chromatograph Procedure" by Fred Stump, ESRL, Environmental Protection Agency, Research Triangle Park, North Carolina.

THIS PROCEDURE IS REPRINTED FROM EPA REPORT EPA 600/2-79-017, "ANALYTICAL PROCEDURES FOR CHARACTERIZING UNREGULATED POLLUTANT EMISSIONS FROM MOTOR VEHICLES." (Reference 3)

APPENDIX A-5

MEASUREMENT OF METHANOL

The measurement of methanol in exhaust is accomplished by bubbling the exhaust through glass impingers containing deionized water. The exhaust sample is collected continuously during the test cycle. For analysis, a portion of the aqueous solution is injected into a gas chromatograph equipped with a flame ionization detector (FID). External methanol standards in deionized water are used to quantify the results. Detection limits for this procedure are on the order of 0.06 ppm in dilute exhaust.

SAMPLING SYSTEM

Two glass impingers in series, with each containing 25 mℓ of deionized water are used to collect exhaust samples for the analysis of methanol. A flow schematic of the sample collection system is shown in Figure 1. The two glass impingers collect 99 percent of the methanol in exhaust. The temperature of the impinger is maintained at 0-5°C by an ice water bath, and the flow rate through the impinger is maintained at 4ℓ/minute by the sample pump. A dry gas meter is used to determine the total flow through the impinger during a given sampling period. The temperature of the gas stream is monitored by a thermocouple immediately prior to the dry gas meter. A drier is included in the system to prevent condensation in the pump, flowmeter, dry gas meter, etc. The flowmeter in the system allows continuous monitoring of the sample flow to insure proper flow rates during the sampling. Several views of the sampling system are shown in Figure 2.

ANALYTICAL PROCEDURE

The analysis of methanol is accomplished by collecting methanol in deionized water and analyzing the sample with a gas chromatograph equipped with an FID. The analysis flow schematic for methanol is shown in Figure 3. A detailed description of the procedure follows.

For the analysis of methanol, dilute exhaust is bubbled through two glass impingers each containing 25 mℓ of deionized water. Upon completion of each driving cycle, the impinger is removed and the contents are transferred to a 30 mℓ polypropylene bottle, and capped.

A Perkin-Elmer 3920B gas chromatograph equipped with a flame ionization detector is used to analyze the sample. A 5 µℓ portion of the sample is injected into the gas chromatograph (GC). The column is a 3' X 1/8" Teflon column containing 120/150 mesh Porapak Q. The carrier gas is helium which flows through the column at a rate of 20 mℓ/minute. The column temperature is maintained at 100°C. A chromatogram of a standard sample containing 63 ppm methanol is shown in Figure 4. To

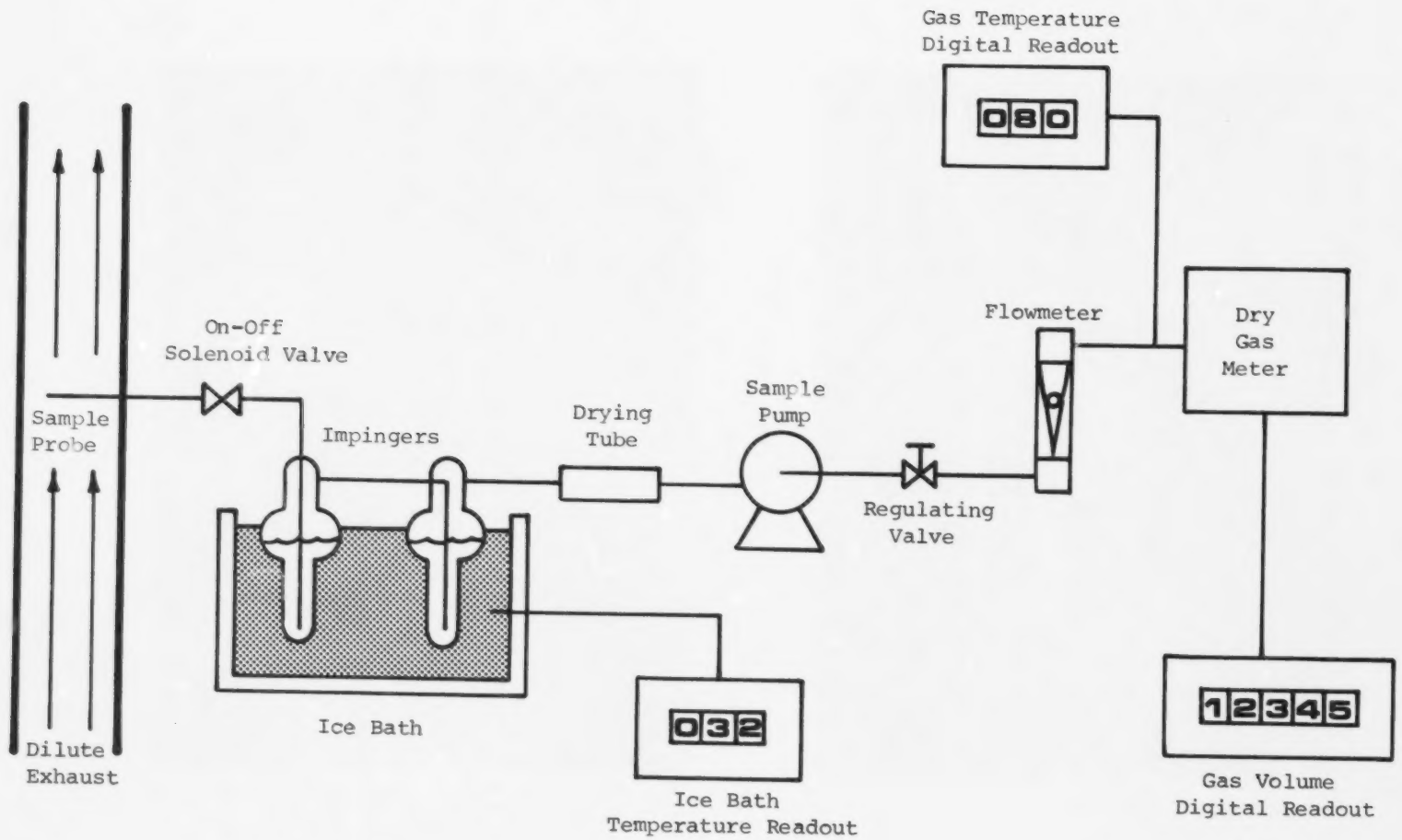
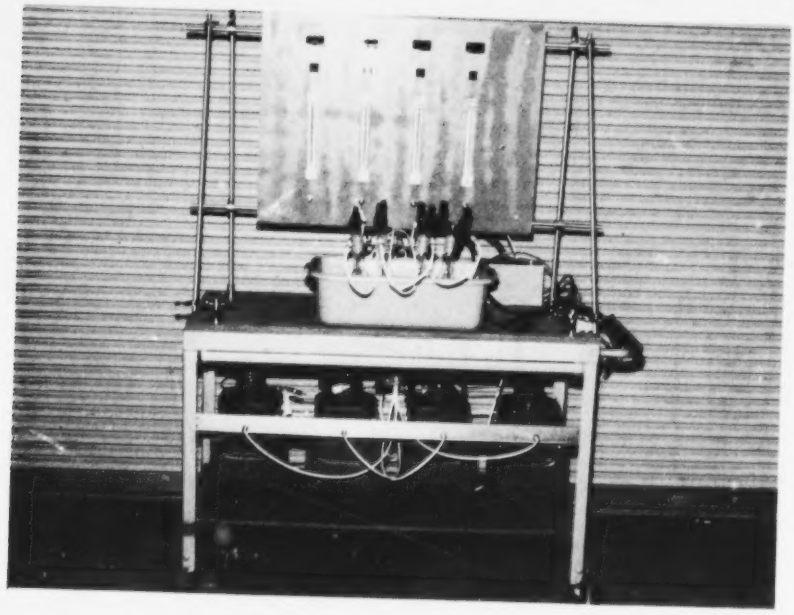
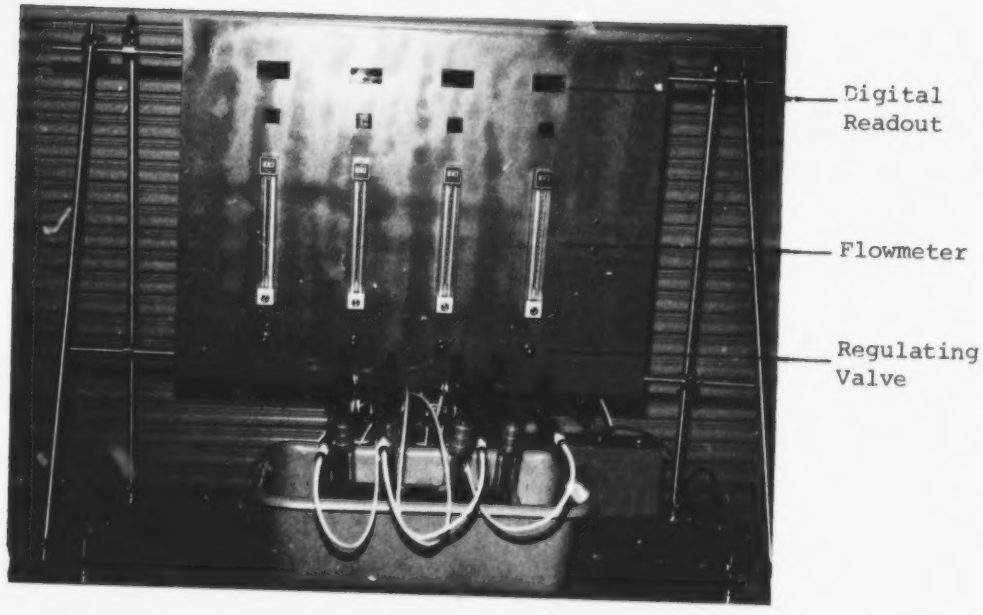


Figure 1. Methanol sample collection flow schematic.

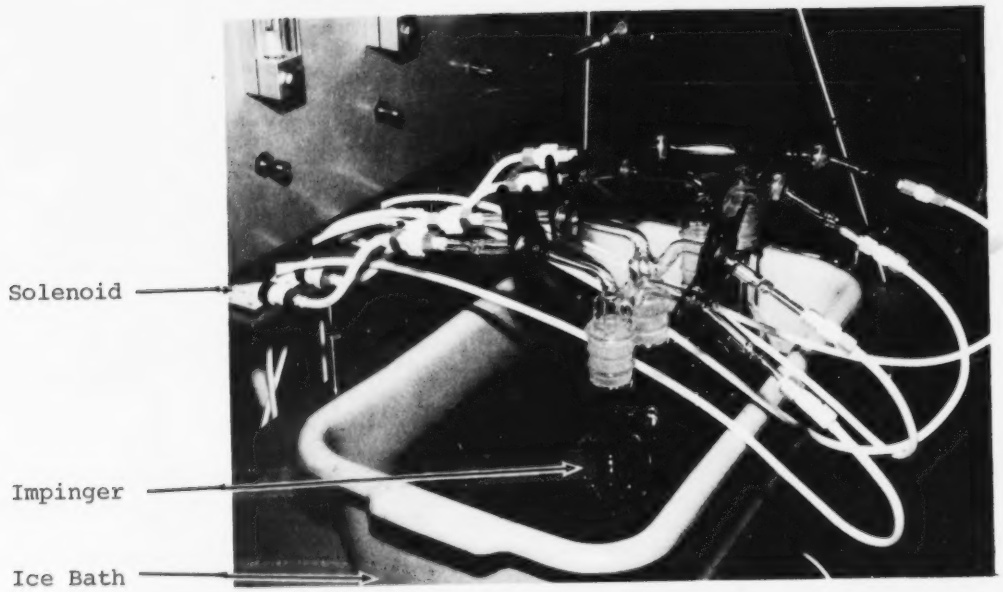


Front View

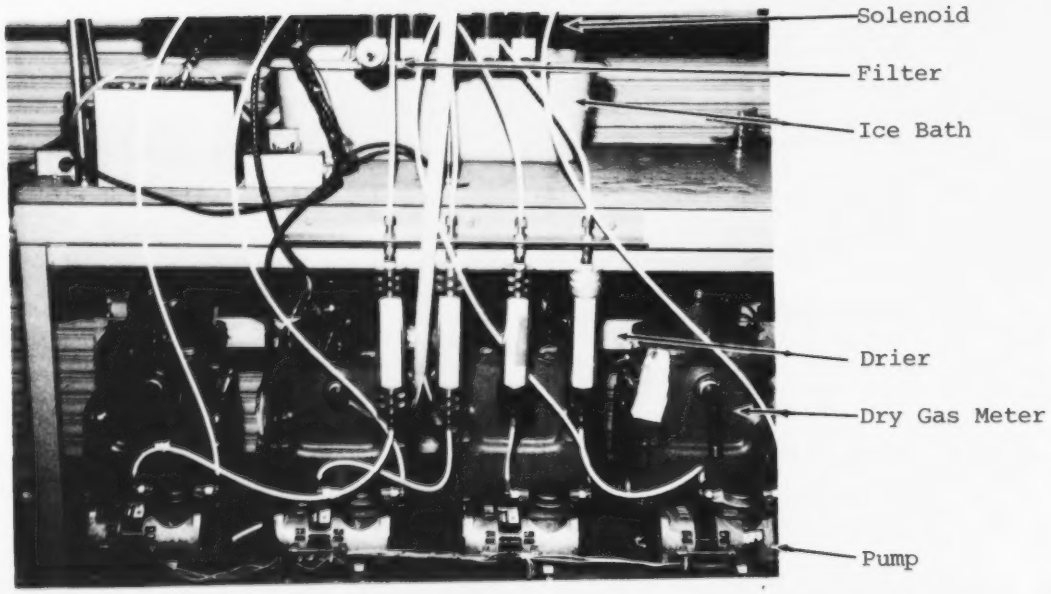


Close-up of Upper Front

Figure 2. Methanol sampling system.



Close-up of Impingers (Side View)



Rear View

Figure 2 (Cont'd). Methanol sampling system.

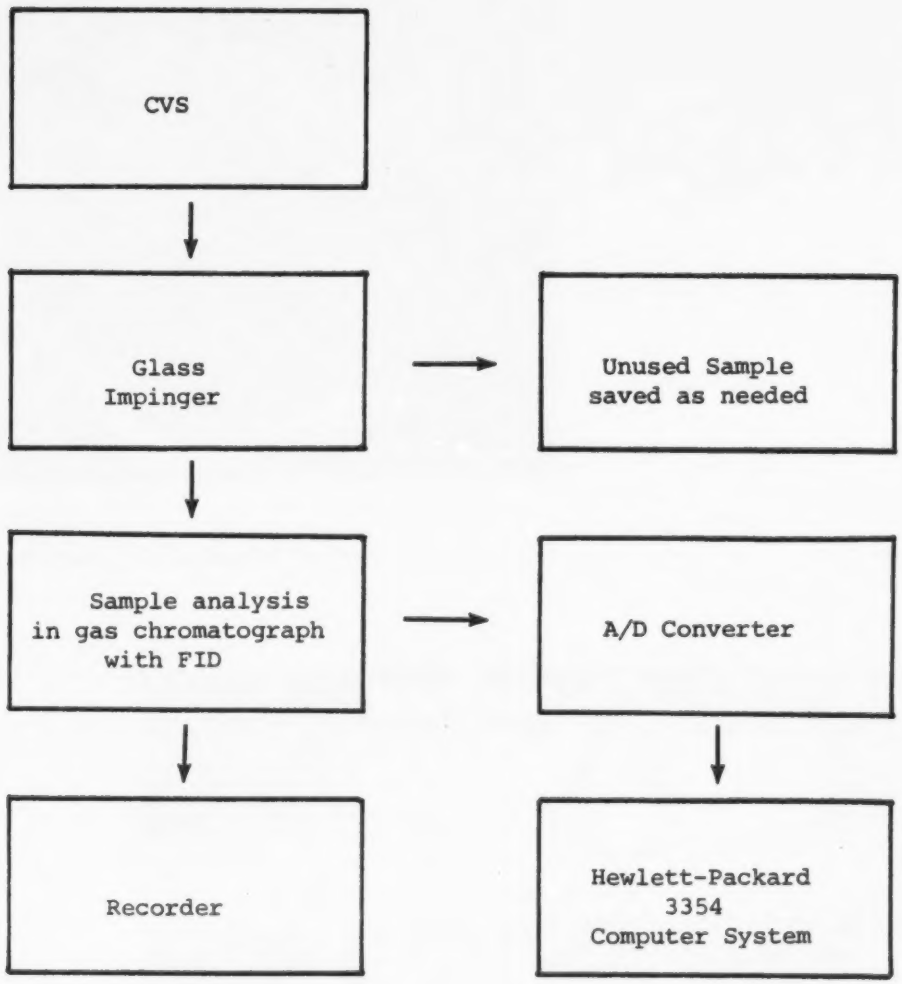


Figure 3. Methanol analysis flow schematic.

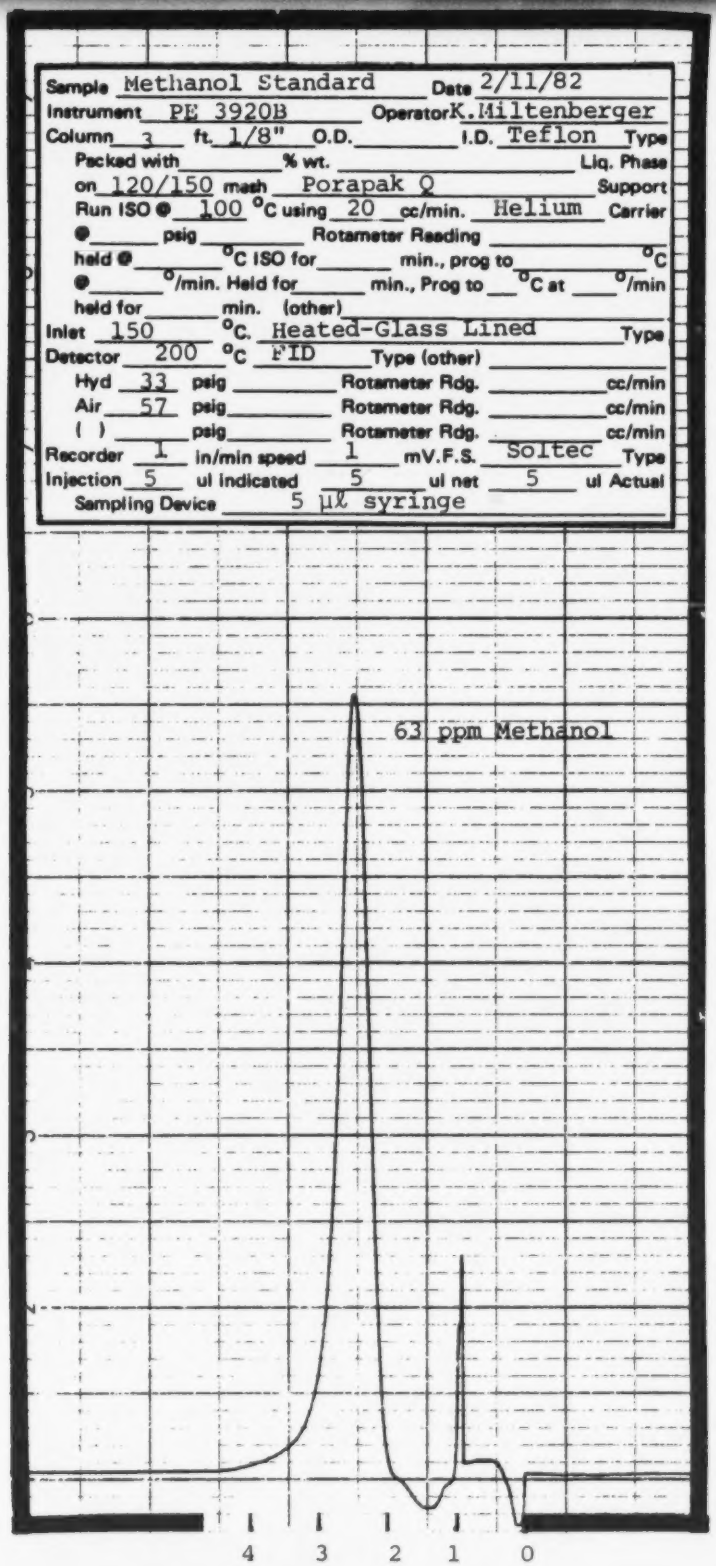

Sample Methanol Standard Date 2/11/82
Instrument PE 3920B Operator K. Miltenberger
Column 3 ft. 1/8" O.D. I.D. Teflon Type
Packed with % wt. Liq. Phase
on 120/150 mesh Porapak Q Support
Run ISO @ 100 °C using 20 cc/min. Helium Carrier
@ psig Rotameter Reading
held @ °C ISO for min., prog to °C
@ °/min. Held for min., Prog to °C at °/min
held for min. (other)
Inlet 150 °C. Heated-Glass Lined Type
Detector 200 °C FID Type (other)
Hyd 33 psig Rotameter Rdg. cc/min
Air 57 psig Rotameter Rdg. cc/min
( ) psig Rotameter Rdg. cc/min
Recorder 1 in/min speed 1 mV.F.S. Soltec Type
Injection 5 ul indicated 5 ul net 5 ul Actual
Sampling Device 5 µℓ syringe
63 ppm Methanol
4
3
2
1
0
Retention time, min.

Figure 4. Chromatogram of methanol standard

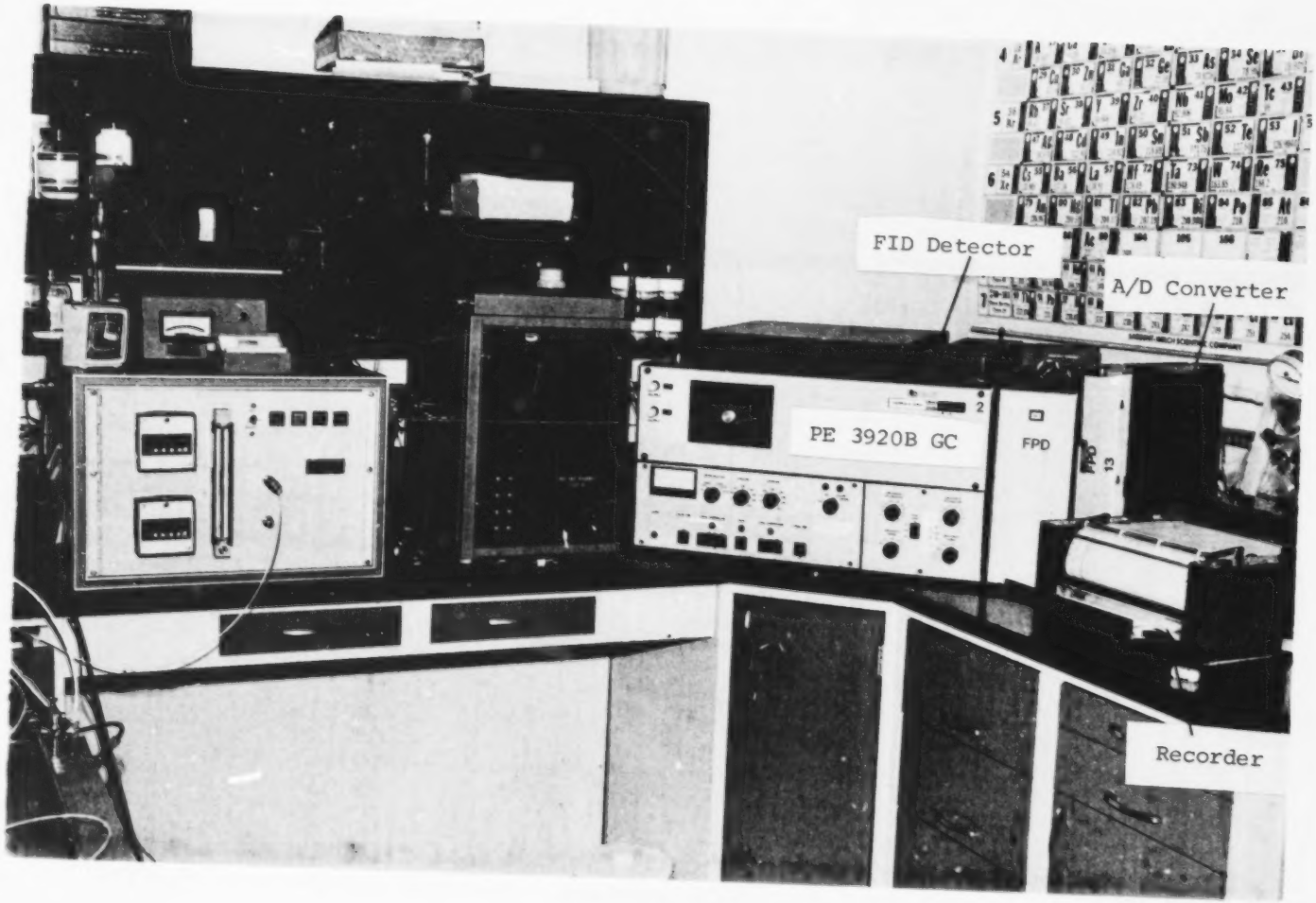


Figure 5. Methanol Analytical system.

quantify the results, the sample peak area is compared to the peak area of a standard solution. Figure 5 shows the analytical system with gas chromatograph, detector, A/D converter, and recorder.

CALCULATIONS

The procedure has been developed to provide the user with the concentration of methanol in exhaust. The results will be expressed in $\mu g/m^3$ of exhaust and ppm. The equations for determining the concentrations in $\mu g/m^3$ and ppm are derived in the following manner.

The first step is to correct the volume of exhaust sampled to a standard temperature, 68°F, and pressure, 29.92"Hg, by use of the equation

$$\frac{P_{exp} \times V_{exp}}{T_{exp}} = \frac{P_{corr} \times V_{corr}}{T_{corr}}$$

V_{exp} = experimental volume of gas sampled in ft^3
V_{corr} = volume of gas sampled in ft^3 corrected to 68°F and 29.92"Hg
P_{exp} = experimental barometric pressure
P_{corr} = 29.92"Hg
T_{exp} = experimental temperature in °F + 460
T_{corr} = 68°F + 460 = 528°R

Solving for V_{corr} gives:

$$V_{corr} = \frac{P_{exp}(\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp}\ (°R) \times 29.92\text{"Hg}}$$

The next step converts the volume from cubic feet to cubic meters by use of the conversion factor: 1 cubic meter is equal to 35.31 cubic feet.

$$V_{corr\,(m^3)} = \frac{P_{exp}\ (\text{"Hg}) \times V_{exp}\ (ft^3) \times 528°R}{T_{exp} \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}$$

(Equation 1)

The next step is to find the concentration of methanol in $\mu g/m\ell$. Since the gas chromatograph FID has a linear response in the concentration of concern, then the following equation holds.

$$\frac{C_{sam}\ (\mu g/m\ell)}{A_{sam}} = \frac{C_{std}\ (\mu g/m\ell)}{A_{std}}$$

C_{sam} = concentration of the sample in µg/mℓ
A_{sam} = GC peak area of sample in relative units
C_{std} = concentration of the standard in µg/mℓ
A_{std} = GC peak area of standard in relative units

Solving for C_{sam} gives:

$$C_{sam}(\mu g/m\ell) = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam}}{A_{std}}$$

The $C_{sam}(\mu g/m\ell)$ in solution is corrected for any necessary dilution by multiplying by the dilution factor, D.F.

$$C_{sam}(\mu g/m\ell) = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times D.F.}{A_{std}}$$

To obtain the total amount in µg of methanol in the aqueous absorbing solution, the absorbing reagent volume is multiplied by the concentration to give:

$$\mu g\ sample = C_{sam}\ (\mu g/m\ell) \times Abs.\ Vol.\ (m\ell)$$

$$= \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times D.F. \times Abs.\ Vol.\ (m\ell)}{A_{std}}$$

(Equation 2)

To obtain µg sample/m^3, Equation 2 is divided by Equation 1 to give:

$$\mu g\ samp/m^3 = \frac{C_{std}\ (\mu g/m\ell) \times A_{sam} \times D.F. \times Abs.\ Vol.\ (m\ell)}{A_{std} \times P_{exp}\ (\text{"Hg}) \times 528^\circ}$$

$$\times \frac{T_{exp} \times 29.92\text{"Hg} \times 35.31\ (ft^3/m^3)}{V_{exp}\ (ft^3)}$$

(Equation 3)

To find the concentration of methanol in ppm, the density of the methanol is needed. At 29.92"Hg and 32°F, one mole of gas occupies 22.4 liters. This volume is corrected to 68°F from the equation

$$\frac{V}{T} = \frac{V_1}{T_1}$$

V_1 = 22.4ℓ
T_1 = 32°F + 460 = 492°R
V = volume at 68°F
T = 68°F + 460 = 528°R

Solving for V gives:

$$V = \frac{V_1 \times T}{T_1} = \frac{22.4 \times 528}{492} = 24.04\ell$$

Since one mole of gas occupies 22.04ℓ at 68°F, the density can be found in g/ℓ by dividing the molecular weight in g/mole by 22.04 ℓ/mole

$$\text{den } (g/\ell) = \frac{\text{mol. wt. g/mole}}{24.04\ \ell/\text{mole}}$$

The density in µg/mℓ can be found by converting g to µg and ℓ to mℓ as follows:

$$\text{den } \mu g/m\ell = \frac{\text{mol. wt. g/mole}}{24.04\ \ell/\text{mole}} \times \frac{1 \times 10^6 \mu g/g}{1 \times 10^3 m\ell/\ell} = \frac{\text{mol. wt. x } 1000}{24.04}$$

(Equation 4)

To obtain the concentration of methanol in ppm, the concentration in $\mu g/m^3$ is divided by the density in µg/mℓ

$$\text{ppm} = \mu g/m^3 \div \mu g/m\ell = \frac{m\ell}{m^3}$$

Using Equations 3 and 4 gives the ppm concentration in the form of the raw data.

$$ppm = \frac{24.04(\ell) \times C_{std}\ (\mu g/m\ell) \times A_{sam} \times D.F. \times Abs.\ Vol.\ (m\ell)}{Mol.\ Wt.\ (g/mole) \times 1000 \times A_{std} \times P_{exp}\ ("Hg)}$$

$$\times \frac{T_{exp}(°R) \times 29.92"Hg \times 35.31\ ft^3/m^3}{528°R \times V_{exp}\ (ft^3)}$$

(Equation 5)

At this point, the concentration can be expressed in $\mu g/m^3$ (Equation 3) and ppm (Equation 5) at 68°F and 29.92"Hg from the raw data.

Hewlett-Packard Calculations

In order to insure maximum turnaround in a minimum time period, a Hewlett-Packard 67 program was developed to calculate the methanol concentrations in $\mu g/m^3$ and ppm from the raw data. This program is presented in Figure 6.

Sample Calculation

Assume exhaust samples were collected in glass impingers for each portion of a three bag 1975 FTP. Raw data for these tests are presented in Figure 7. Calculations were performed using the HP 67 program and manual calculations.

Manual calculations for driving cycle FTP-1

For Bubbler #1

$$\mu g/m^3 CH_3OH = \frac{C_{std}(\mu g/m\ell) \times A_{sam} \times D.F. \times Abs.\ Vol.\ (m\ell)}{A_{std} \times P_{exp}\ ("Hg)}$$

$$\times \frac{T_{exp} \times 29.92"Hg \times 35.31\ ft^3/m^3}{528°R \times V_{exp}\ (ft^3)}$$

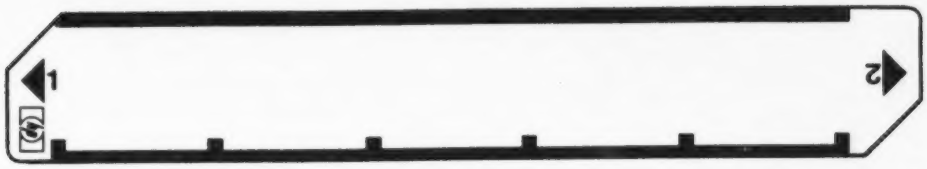
$$= \frac{(7.9\ \mu g/m\ell) \times 1000 \times 1 \times 25}{1500 \times 29.80"Hg}$$

$$\times \frac{(460 + 75) \times 29.92"Hg \times 35.31\ ft^3/m^3}{528°R \times 3.196\ ft^3}$$

$$= 1480\ \mu g/m^3$$

Figure 6. HP-67

User Instructions



STEP	INSTRUCTIONS	INPUT DATA/UNITS	KEYS		OUTPUT DATA/UNITS
0_1	Switch to on; switch to run				
0_2	Feed side 1 of card in from right to left				
0_3	Set decimal place		g	Sci	
1	Input Sample Volume	ft^3	A		
2	Input Barometric Pressure	"Hg	R/S		
3	Input Sample Temperature	°F	R/S		
4	Input Absorbing Reagent Volume	mℓ	R/S		
5	Input Dilution Factor, Bubbler #1		R/S		
6	Input Standard Concentration, Bubbler #1	µg/mℓ	R/S		
7	Input Standard Area, Bubbler #1	counts	R/S		
8	Input Sample Area, Bubbler #1	counts	R/S		
9	Output Sample Conc., Bubbler #1				µg/mℓ
10	Input Dilution Factor, Bubbler #2		R/S		
11	Input Standard Conc., Bubbler #2	µg/mℓ	R/S		
12	Input Standard Area, Bubbler #2	counts	R/S		
13	Input Sample Area, Bubbler #2	counts	R/S		
14	Output Sample Conc, Bubbler #2		R/S		µg/mℓ
15	Output Sample Conc., Bubbler # 1 & #2		R/S		µg/mℓ
16	Output Sample Conc.				ppm
			h	RTN	

Figure 6 (Cont'd). HP-67 Program Form

STEP	KEY ENTRY	KEY CODE	COMMENTS
001	f LBL A	31 25 11	In Sample Vol., ft^3
	2	02	
	÷	81	
	R/S	84	In Barometric Pressure, "Hg
	X	71	
	STO 1	33 01	
	R/S	84	In Sample Temp, °F
	4	04	
	6	06	
010	0	00	
	+	61	
	RCL 1	34 01	
	÷	81	
	R/S	84	In Sol. Vol., mℓ
	X	71	
	STO 2	33 02	
	RCL 2	34 02	
	R/S	84	In Dilution Factor
	X	71	
020	R/S	84	In Std Conc., µg/mℓ
	X	71	
	R/S	84	In Std. Area
	÷	81	
	R/S	84	In Sample Area, Bubbler #1
	X	71	
	STO 3	33 03	
	R/S	84	Out Sample Conc, Bubbler#1, $\mu g/m^3$
	RCL 2	34 02	In Dilution Factor
	X	71	
030	R/S	84	In Std. Conc., µg/mℓ
	X	71	
	R/S	84	Input Std. Area
	÷	81	
	R/S	84	In Sample Area, Bubbler #2
	X	71	
	R/S	84	Out Sam. Conc, Bubbler #2, $\mu g/m^3$
	RCL 3	34 03	
	+	61	
	R/S	84	
040	1	01	Out Conc., $\mu g/m^3$
	3	03	
	3	03	
	3	03	
	÷	81	
	R/S	84	Output ppm Methanol
	h RTN	35 22	
050			

STEP	KEY ENTRY	KEY CODE	COMMENTS
060			
070			
080			
090			
100			
110			

REGISTERS

0	1	2	3	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9

A	B	C	D	E	I

Figure 6 (Cont'd). HP-67 Program Form

STEP	KEY ENTRY	KEY CODE	COMMENTS
001	f LBL A	31 25 11	In Sample Vol., ft^3
	2	02	
	÷	81	
	R/S	84	In Barometric Press-
	X	71	ure, "Hg
	STO 1	33 01	
	R/S	84	In Sample Temp., °F
	4	04	
	6	06	
010	0	00	
	+	61	
	RCL 1	34 01	
	÷	81	
	R/S	84	In Sol. Vol., mℓ
	X	71	
	STO 2	33 02	
	RCL 2	34 02	
	R/S	84	In Dilution Factor
	X	71	
020	R/S	84	In Std Conc., µg/mℓ
	X	71	
	R/S	84	In Std. Area
	÷	81	
	R/S	84	In Sample Area,
	X	71	Bubbler #1
	STO 3	33 03	
	R/S	84	Out Sample Conc. Bubbler #1, $\mu g/m^3$
	RCL 2	34 02	In Dilution Factor
	X	71	
030	R/S	84	In Std. Conc., µg/mℓ
	X	71	
	R/S	84	Input Std. Area
	÷	81	
	R/S	84	In Sample Area,
	X	71	Bubbler #2
	R/S	84	Out Sample conc.,
	RCL 3	34 03	Bubbler #2, $\mu g/m^3$
	+	61	
	R/S	84	
040	1	01	Out Conc., $\mu g/m^3$
	3	03	
	3	03	
	3	03	
	÷	81	
	R/S	84	Output ppm Methanol
	h RTN	35 22	
050			

STEP	KEY ENTRY	KEY CODE	COMMENTS
060			
070			
080			
090			
100			
110			

REGISTERS

0	1	2	3	4	5	6	7	8	9
S0	S1	S2	S3	S4	S5	S6	S7	S8	S9

A	B	C	D	E	I

METHANOL

SWRI PROJECT NO._____ TEST NO._____ TEST DATE:_____ VEHICLE:_____

FUEL_____ CVS NO._____ TUNNEL SIZE:_____ DRIVER:_____ MILES:_____

SAMPLE COLLECTION BY: _____ CHEMICAL ANALYSIS BY:_____ CALCULATIONS BY:_____

GENERAL COMMENTS_____

Test No.	1	2	3	4	5	6
Driving Cycle	FTP-1	FTP-1	FTP-3	SET-7	HFET	NYCC
Volume, Ft^3	3.196	1.625	2.010	3.730	8.241	1.070
B.P., "Hg	29.80	30.02	29.02	29.25	29.95	29.50
Temp. °F	75	80	96	85	83	89
Absor. Rea. Vol., mℓ	25	25	50	50	75	75
Dilution Factor, Bubbler #1	1	5	10	2	1	1
Std. Conc $\mu gCH_3OH/m\ell$ Bub. #1	7.9	79	790	7.9	7.9	0.79
Std. Area - Bubbler #1	1500	5000	10000	1000	5000	1000
Sample Area - Bubbler #1	1000	1000	1000	3000	15000	3000
Sample Conc $\mu gCH_3OH/m^3$, Bub#1	1480	43700	753000	23700	7820	6180
Dilution Factor, Bubbler #2	1	2	5	1	1	1
Std. Conc $\mu gCH_3OH/m\ell$ Bub. #2	0.79	7.9	7.9	0.79	0.79	0.79
Std. Area - Bubbler #2	2000	1500	5000	1000	6000	5000
Sample Area - Bubbler #2	500	300	6000	100	1000	15000
Sample Conc $\mu gCH_3OH/m^3$, Bub#2	55.5	1750	45200	39.5	43.5	6180
Total Conc. $\mu gCH_3OH/m^3$	1530	45500	798000	23700	7860	12400
PPM Methanol	1.15	34.1	599	17.8	5.90	9.28

Figure 7. Methanol sample collection sheet

The concentration in Bubbler #2 is calculated in the same manner using the appropriate dilution factor, standard concentration, standard area, and sample area:

For Bubbler #2:

$$\mu g/m^3 = \frac{0.79\ \mu g/m\ell \times 500 \times 1 \times 25}{2000 \times 29.80}$$

$$\times \frac{(460 + 75) \times 29.92\text{"Hg} \times 35.31\ ft^3/m^3}{528°R \times 3.196\ ft^3}$$

$$= 55.5\ \mu g/m\ell^3$$

The concentrations from the two bubblers can be added for a total concentration:

$$\text{Total } \mu g \text{ methanol}/m^3 = \text{conc.(Bubbler \#1)} + \text{conc.(Bubbler \#2)}$$
$$= 1480\ \mu g/m^3 + 55.5\ \mu g/m^3$$
$$= 1535\ \mu g/m^3$$

$$PPM\ CH_3OH = \mu g/m^3 \div \text{density } \mu g/m\ell$$

$$\text{density } \mu g/m\ell = \frac{\text{Mol. Wt. } (CH_3OH) \times 1000}{24.04\ell}$$

$$\text{Mol. Wt. } CH_3OH = 32.04\ g/mole$$

$$\text{density} = \frac{32.04 \times 1000}{24.04\ell} = 1333\ \mu g/m\ell$$

$$ppm = 1535 \div 1333\ \mu g/m\ell = 1.15\ m\ell/m^3 = 1.15\ ppm$$

Note: The values used in these calculations are picked from a range of temperatures, standards, dilution factors, etc., to validate the calculations and may not be representative of expected raw data. These calculations are presented to confirm that the manual and HP-67 calculations give the same results. This was confirmed on six sets of calculations.

LIST OF EQUIPMENT AND REAGENTS

The equipment and reagents for the analysis of the methanol is divided into two groups. The first involves the sample acquisition and the second the instrumental analysis of the sample once it has been obtained. Manufacturer, stock number and any pertinent descriptive information are listed. The preparation of standards is also discussed.

Sampling

1. Glass impingers, Ace Glass Products, Catalog #7530-11, plain tapered tip stoppers with 18/7 arm joints and 29/42 bottle joints.

2. Flowmeter, Brooks Instrument Division, Model 1555, tube size R-2-15-C, graduated 0-15, sapphire float, 0-5 ℓ/min range.

3. Sample pump, Thomas Model 106 CA18, capable of free flow capacity of 4 ℓ/min.

4. Dry gas meter, American Singer Corporation, Type AL-120, 60 CFH capacity.

5. Regulating valve, Nupro 4MG, stainless steel.

6. Teflon tubing, United States Plastic Corporation, 1/4" OD x 1/8" ID and 5/16" OD x 1/8" ID.

7. Teflon solenoid valve, the Fluorocarbon Company, Model DV2-144NCA1.

8. Drying tube, Analabs Inc., Catalog #HGC-146, 6" long, 1/4" brass fittings.

9. Miscellaneous Teflon nuts, ferrules, unions, tees, clamps, connectors, etc.

10. Digital readout for dry gas meter.

11. Miscellaneous electrical switches, lights, wirings, etc.

12. Six channel digital thermometer, Analog Devices, Model #2036/J/1.

13. Iron/Constantan type J single thermocouple with 1/4" OD stainless steel metal sheath, Thermo Sensors Corporation.

14. 30 mℓ polypropylene sample storage bottles, Nalgene Labware, Catalog #2006-0001.

15. Deionized or distilled water.

16. Class A, 10 mℓ volumetric pipet.

17. Class A, 1000 mℓ volumetric flask.

Instrumental Analysis

1. 5 µl syringe, Hamilton Co., Reno, Nevada.

2. Perkin-Elmer Model 3920 B gas chromatograph equipped with flame ionization detector.

3. Soltec Model B-281 1 mv recorder.

4. Hewlett-Packard Model 3354 gas chromatograph computer system with remote teletype printout.

Preparation of Primary Standards

The primary standard for the methanol analysis is prepared by diluting a known volume of methanol with deionized (or distilled) water. Standards less than ∿500 ppm are prepared by diluting higher concentration standards with deionized water.

THIS PROCEDURE IS REPRINTED FROM EPA REPORT EPA 460/3-82-004, "CHARACTERIZATION OF EXHAUST EMISSIONS FROM METHANOL AND GASOLINE FUELED AUTOMOBILES." (Reference 5)

APPENDIX A-6

MEASUREMENT OF ETHANOL

The measurement of ethyl alcohol in exhaust and evaporative emissions was accomplished by direct bag analysis using a gas chromatograph equipped with a flame ionization detector. A limited number of qualification and validation experiments were conducted to insure the accuracy and reliability of the procedure. Contacts were made with key individuals at EPA, Ann Arbor and Research Triangle Park to coordinate the approach to this analysis with other participants in the evaporative emissions program.

Analytical System

The analysis for ethyl alcohol in exhaust and evaporative emissions is conducted using a gas chromatograph equipped with a flame ionization detector. The system employs two pneumatically operated electrically controlled Seiscor valves, one in a gas sampling valve configuration and the other in the back-flush configuration. Figure A-1 illustrates the flow schematic of the analytical system.

The system was deisgned for bag analysis and used normal CVS bag samples for the exhaust emissions. In the case of the SHED emissions, bag samples were collected during the first and last minute of the soak. These bags were then transported to the gas chromatograph for subsequent analysis.

The analytical column selected for this separation was a 10' x 1/8" SS with 15% TCEP on 60/80 Chromosorb P. The separation of ethyl alcohol from benzene and toluene was satisfactory and no known interferences were encountered. The gas chromatograph oven was maintained at 50°C and the system was backflushed after the toluene peak. The total analysis time was 45-60 minutes. A typical separation of ethyl alcohol and the two closest eluting compounds is presented in Figure A-2. The specific GC operating parameters for this separation is presented in Table A-1.

Control System

The control of the two Seiscor valves is accomplished by ATC timers and ASCO electric solenoid valves. The electrical schematic for the control of the Seiscor valves using these timers and electric solenoid valves is shown in Figure A-3. The flow schematic for the vacuum and pressure lines to the Seiscor valves are presented in Figure A-4.

Equipment

This analysis is performed using a gas chromatograph equipped with a flame ionization detector. The gas chromatograph, recorder and data acquisition system are major components in the detection system. A control console was fabricated to house the mechanical hardware items that are necessary for the proper operation of the ethyl alcohol analysis system. The major items that are included in each of these systems is listed as follows:

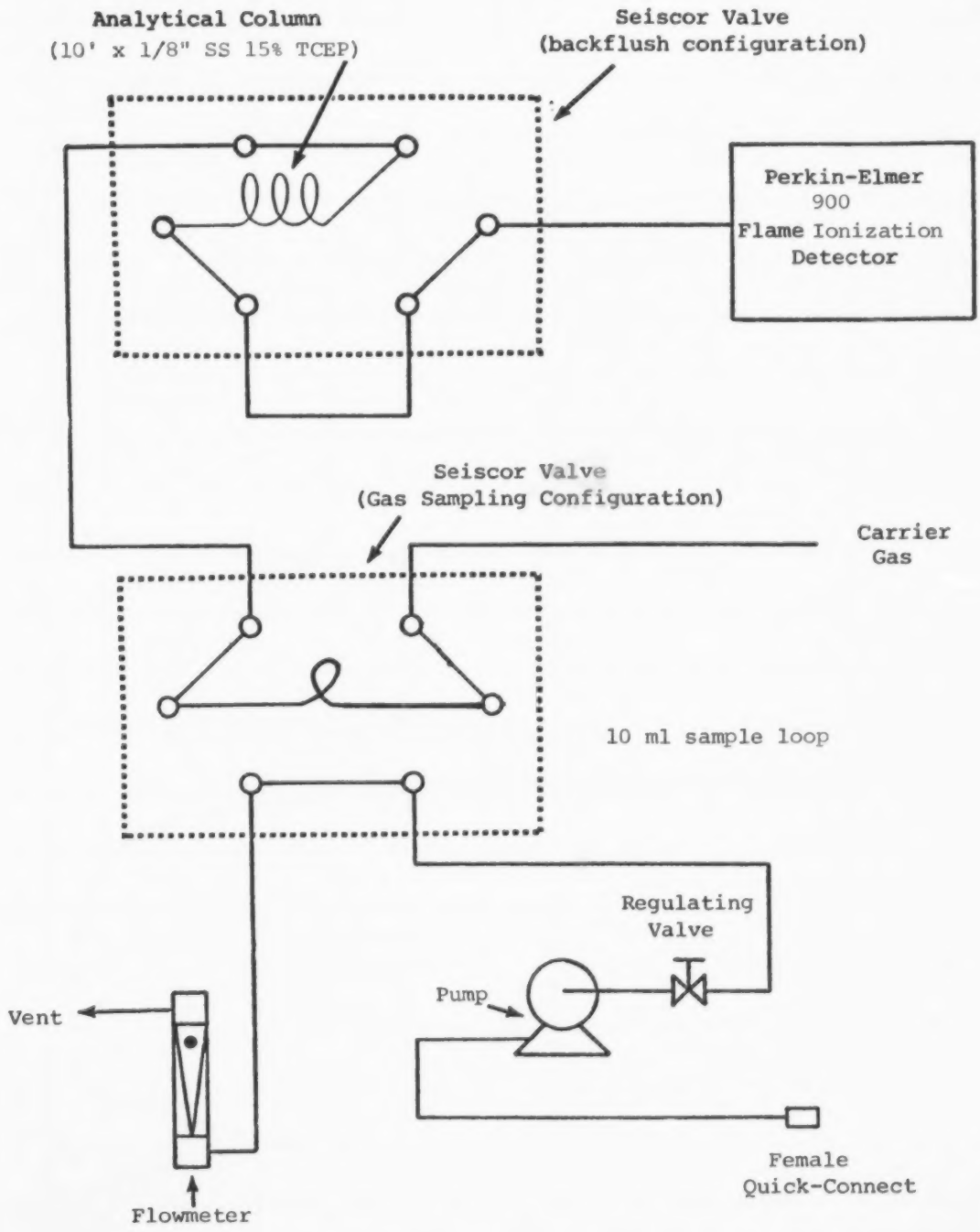


Figure 1. Ethyl Alcohol Analytical Flow Schematic

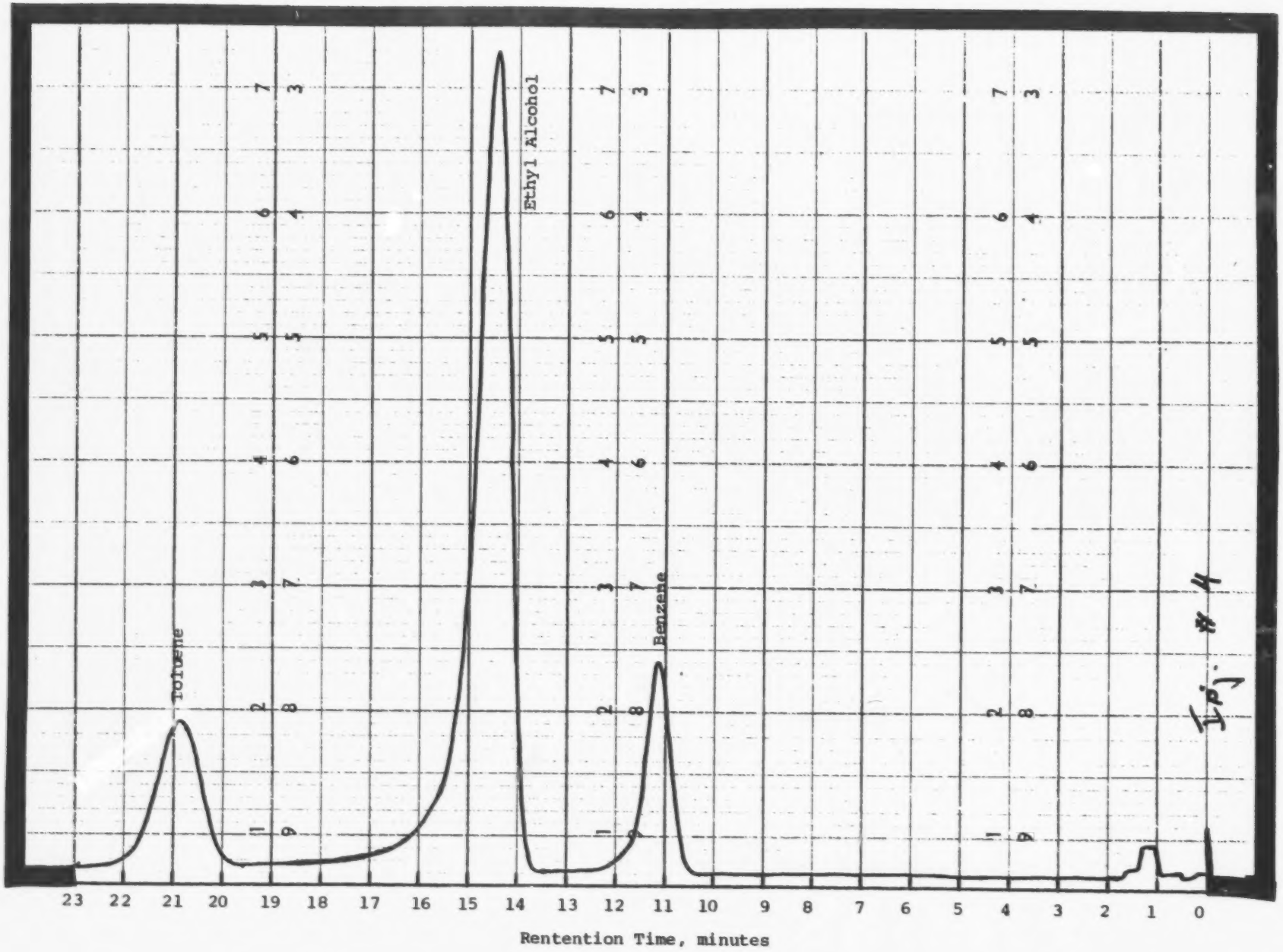


Figure 2. Typical Separation of Ethyl Alcohol from Benzene and Toluene

TABLE 1. ETHYL ALCOHOL ANALYSIS GAS CHROMATOGRAPH OPERATING PROCEDURES

Gas Chromatpgraph:	Perkin-Elmer Model 900
Detector Type:	Flame Ionization Detector
Gas Sampling Valve:	Seiscor Model VIII (GSV Configuration)
Backflush Valve	Seiscor Model VIII (BF Configuration)
Sample Loop Size:	10 ml
Column Temperature:	50°C
Detector Temperature:	50°C
Injection Temperature:	27°C
Carrier Gas:	Helium
Carrier Gas Flow:	30 ml/min
Hydrogen Gas Flow:	40 ml/min
Air Flow Rate:	400 ml/min
Column Dimensions:	10' x 1/8" SS
Column Material:	15% TCEP on 60/80 Chromosorb P-AW

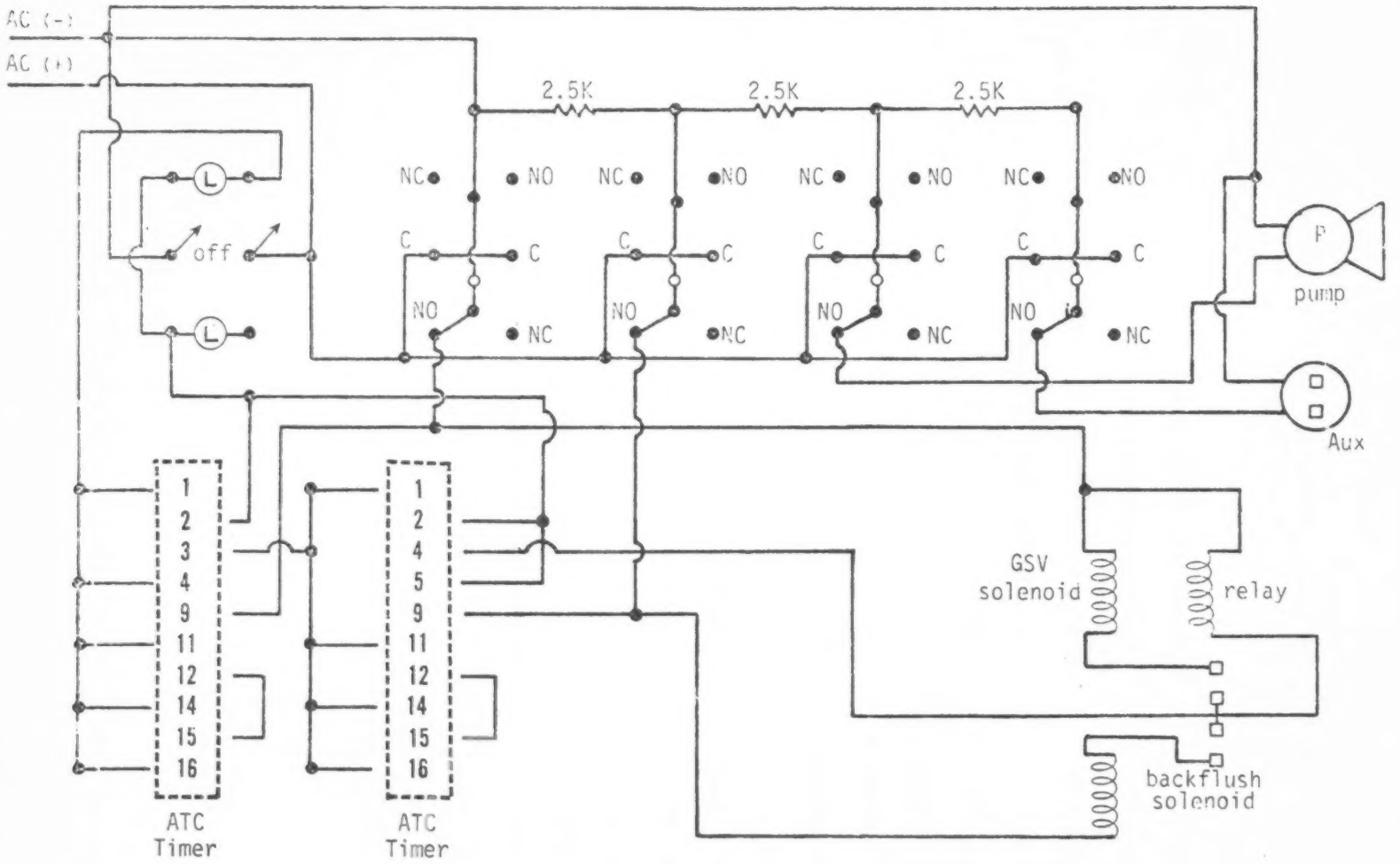


Figure 3. Electrical Schematic for Nitrous Oxide Analysis System

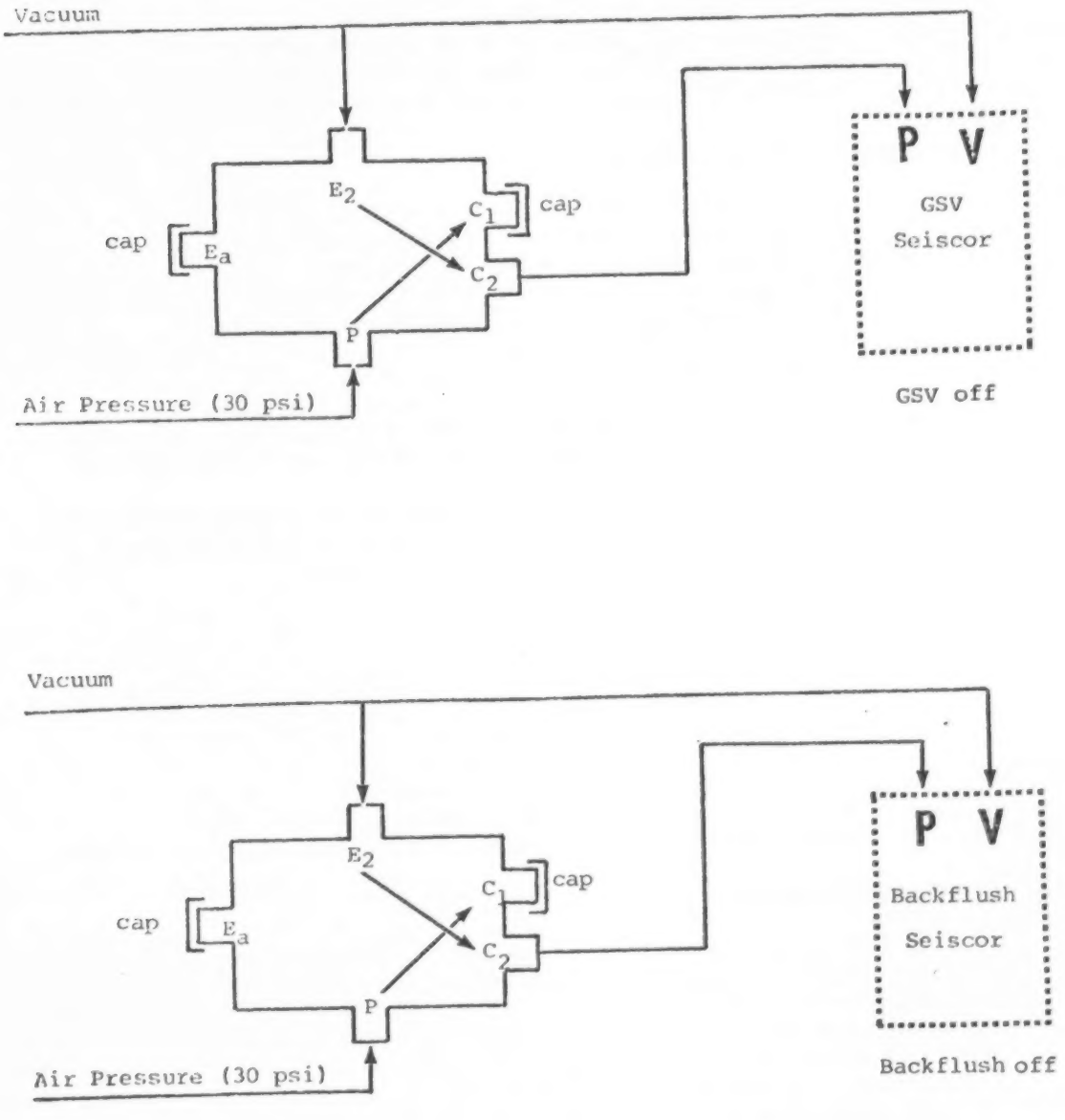


Figure 4. Flow Schematic in Electric Solenoid Valves
(Both valves de-energized)

Gas Chromatograph

1. Perkin-Elmer Model 900 chromatograph
2. Soltec Model B-281 recorder
3. Hewlett-Packard Model 3354C GC computer system
4. Hewlett-Packard Model 1865A A/D Converter
5. Analytical column, 10' x 1/8" SS, 15% TCEP on 60/80 Chromosorb P-AW

Control Console System

1. Seiscor valve - gas sampling configuration
2. Seiscor valve - backflush configuration
3. ATC timers, Model 3254A346A10PX (2 ea)
4. ACSO solenoid valve, Model 834501 (2 ea)
5. Brook flowmeter, R-2-15-A w/SS float, 0-150 scale
6. Metal Bellows MB-155 pump
7. Female quick-connect, stainless steel
8. Nupro Model 2M stainless steel regulating valve
9. Stainless steel tubing (0.01"ID) for capillary restrictor
10. Miscellaneous stainless steel, copper and Telflon tubing (1/8" and 1/16")
11. Miscellaneous stainless steel and brass unions, tees, etc.
12. Bud Classic II control console cabinet, 14" x 19" panel
13. Miscellaneous electrical on-off switches

SHED Bag Sample Acquisition System

1. Sample pump, Thomas Model 917 CA TFE
2. Brooks flowmeter, Model 1555, R-6-15-A, sapphire float, 0-11 lpm
3. Regulating valve, Mupro 4MG, SS
4. Telfon tubing, 1/4" OD x 1/8" ID
5. SS quick connects, male and female
6. Tedlar bag ≈ one cubic foot capacity
7. Miscellaneous nuts, females and assorted unions, tees, etc.

Sample Calculations

It was initially planned to use ethyl alcohol blends in normal calibration cylinders. During the validation of the calibration technique, it became apparent that high pressure ethyl alcohol blends were not stable and other calibration techniques were investigated. Benzene was selected to be used as the external standard and the relative response to ethyl alcohol was established. Experiments determined that 1 ppm C (benzene) was equivalent to 0.05 mg ethanol per cubic foot. Using this relationship, the following equations were used to determine grams of ethanol per test.

1. General Calculation Equation

$$\text{ppm C Ethanol} = \frac{\text{GC area of Ethanol x ppm C Standard (Benzene)}}{\text{GV area standard (benzene)}}$$

2. Ethanol Evaporative Losses

Ethanol g/test - ppm C (0.050 mg/ppm C ft^3) (SHED vol. ft^3) (1 g/10^3mg)

If a test used a 68.3 ppm C benzene standard that gave area counts and the SHED volume was 1708 ft^3, then the following rate would be calculated.

$$\text{ppm C Ethanol} = \frac{(3560 \text{ area counts, } C_2H_5OH)\ (68.3 \text{ ppm C } C_6H_6)}{(17521 \text{ area counts, } C_6H_6}$$

ppm C Ethanol = 13.88 ppm C

Ethanol, g/test = ppm C C_2H_5OH x Response factor x SHED vol.

Ethanol, g/test = 13.88 ppm C x 0.050mg/ppm C ft^3 x 1708 ft^3 x 1g/1000mg

Ethanol, g/test = 1.19 g

THIS PROCEDURE IS REPRINTED FROM A FINAL REPORT TO THE ENVIRONMENTAL PROTECTION AGENCY UNDER CONTRACT NO. 68-03-2377, "GASOHOL, TBA, MTBE EFFECTS ON LIGHT-DUTY EMISSIONS." (Reference 6)

APPENDIX B

B-1. DERIVATION OF EQUATIONS FOR CALCULATION OF EXHAUST EMISSIONS

APPENDIX B-1

DERIVATION OF EQUATIONS FOR CALCULATION OF EXHAUST EMISSIONS

The derivations are given in the order of occurrence of the equation in Section IV.B. of this report. Atmospheric values and atomic weight utilized are:

Standard Atmosphere (11)

Molecular Wt. = 28.966
O_2% by Vol. = 20.95 (23.14 by weight)
O_2 Mol. Wt. = 32.000
N_2+ % of Vol. = 79.05 (76.86 by weight)
N_2+ Mol. Wt. = 28.162

Where N_2+ = Sum of all elements other than oxygen

Atomic Weights (11)

Carbon (C) = 12.011
Hydrogen (H) = 1.0079 (use 1.008)
Oxygen (O) = 15.9994 (use 16.000)

Exhaust Organic Matter Density:

$Density_{HC}$ = 16.33 g/ft^3 for carbon-to-hydrogen ratio of 1:1.85
Fuel Fraction Carbon for 1:1.85 = (1×12.011)/(1×12.011 + 1.85×1.008) = 0.8656
HC Molecular Weight per Carbon Atom = 12.011/FFC
Density OM = 16.33×Ratio of Mol. Wts.
= 16.33 ((12.011/EFC)/(12.011/0.8656))
= 14.135/EFC g/ft^3 (0.4493/EFC kg/m^3)

(c)(3) CO_{mass} = CARBON MONOXIDE EMISSIONS

Hydrogen-to-Carbon Ratio of Fuel (HCR)

HCR = Atoms of H/Atoms of C
= Ratio of weight amounts in fuel/Ratio of mol. wt.
= (FFC/FFC)/(1.008/12.011)
HCR = (FFH/1.008)/(FFC/12.011)

CO Correction for Water Vapor

Total H_2O = Water Due to Combustion + Humidity

$H_2O_{comb} \simeq HCR \times CO_{2c}/2$

Therefore:

$$CO_c = (1 - 0.01 + 0.005 \times HCR \times CO_{2c} - 0.000323F) \times CO_{cm}$$

(c)(5) DF = Stoichiometric Percent CO_2/Summation of Carbon Containing Exhaust Components

Combustion Balance

$$C + H + O + X + O_2 + N_2{+} = CO_2 + H_2O + X + N_2{+}$$

$N_2{+}$ = Summation of all components in the atmosphere except oxygen

Number of Atoms$\propto$Relative Weight/Atm. Wt.
Number of Molecules$\propto$Relative Weight/Mol. Wt.

Therefore:

$$\frac{FFC}{12.011} + \frac{FFH}{1.008} + \frac{FFO}{16.000} + \frac{FFX}{MWX} + \frac{SAFR\times 0.2314}{32.000} + \frac{SAFR\times 0.7686}{28.162} =$$

$$\frac{FFC}{12.011} + \frac{0.5\times FFH}{1.008} + \frac{FFX}{MWX} + \frac{SAFR\times 0.7686}{28.162}$$

SARF = Stoichiometric Air to Fuel Ratio by Weight

Oxygen Balance (Number of Atoms)

$$\frac{2\times FFC}{12.011} + \frac{0.5\times FFH}{1.008} - \frac{FFO}{16.000} = \frac{2\times SAFR\ 0.2314}{32.000}$$

$$SARF = 11.514\times FFC + 34.298\times FFH - 4.322\times FFO$$

Stoichiometric Percent CO_2

$$SPCO_2 = (\text{Exhaust } CO_2/\text{Total Exhaust})\times 100$$
$$= ((FFC/12.011)/(FFC/12.011 + 0.5\times FFH/1.008 + FFX/MWX + SAFR\times 0.7686/28.162))\times 100$$
$$= (FFC/(FFC + 5.958\times FFH + 12.011\times FFX/MWX + 0.3278\times SAFR))\times 100$$

Dilution Factor

$$DF = SPCO_2/[CO_{2c} + (OM_c + CO_c)\times 10^{-4}]$$

Where:

OM_c = Organic matter in ppm carbon equivalent

APPENDIX C

C-1. DERIVATION OF ENERGY BASED FUEL CONSUMPTION
C-2. DERIVATION OF EQUATIONS FOR CALCULATION OF EVAPORATIVE EMISSIONS

APPENDIX C-1

DERIVATION OF ENERGY BASED FUEL CONSUMPTION

$$EBFC = (1/FE) \times (3785.4 \times FDEN/453.6) \times LHV$$
$$= 8.345 \times FD \times LHV/FE$$

Where:

- ESFC = Energy based fuel consumption, Btu/mile
- FDEN = Fuel density, g/mℓ
- LHV[a] = Lower heating value of the fuel, Btu/lb
- FE = Fuel economy, mpg
- 3785.4 = Conversion from gallon to mℓ
- 453.6 = Conversion from pound to gram

---

[a] The lower heating value has been used so as to be in agreement with the normal usage for engines.

APPENDIX C-2

DERIVATION OF EQUATIONS FOR CALCULATION OF EVAPORATIVE EMISSIONS

$$M_{OM} = MW_{OM}/MW_{AIR} \times ppmC \times 10^{-6} \times V_n \times DEN_{AIR} \times C_T \times C_P$$

Where:
MW_{OM} = Molecular Weight of organic matter per carbon atom
MW_{AIR} = 28.966
V_n = Net Volume of the Enclosure, ft^3
DEN_{AIR} = 34.69 g/ft^3
C_T = 518.7/T; T = °R
C_P = P_B/29.92 P_B = in. Hg

$$M_{OM} = (0.208\ MW_{OM}) \times V_n \times (ppmC \times Baro/Temp) \times 10^{-4}$$

Let:
K = $0.208 \times MW_{OM}$
C = ppmC×Baro/Temp

Then:
$M_{OM} = KV_n \times 10^{-4} (C_f - C_i)$